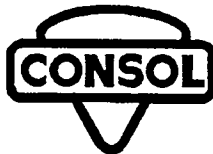


ADVANCED IN-DUCT SORBENT INJECTION FOR SO₂ CONTROL

TOPICAL REPORT NO. 5 TASK 4: DATA ANALYSIS AND COMPUTER MODELING

J. T. Maskew
W. A. Rosenhoover
J. A. Withum
M. R. Stouffer

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CONSOL Inc.
Research & Development
4000 Brownsville Road
Library, PA 15129

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**ADVANCED IN-DUCT SORBENT INJECTION FOR SO₂ CONTROL,
DOE CONTRACT DE-AC22-91PC90360,
TOPICAL REPORT NO. 5, TASK 4: DATA ANALYSIS AND COMPUTER MODELING**

ABSTRACT

The objective of this research project is to develop a second generation in-duct sorbent injection technology as a cost-effective compliance option for the 1990 Clean Air Act Amendments. Specific performance targets are 90% SO₂ removal and 60% sorbent utilization efficiency. After initial results indicated that the Advanced Coolside process had a potential of exceeding these targets, research focused on the Advanced Coolside process.

For Task 4, Data Analysis and Computer Modeling, the objective was to develop two computer models. The first computer model would correlate sorbent properties with hydration parameters, while the second would correlate desulfurization performance with the sorbent properties. A two-level factorial program was undertaken to examine the effects of selected hydration process variables on some of the physical and chemical properties of the hydrates produced and on their SO₂ reactivity. A bench-scale hydrator was used to convert quicklime samples to hydrated limes under controlled processing conditions. Two quicklimes were hydrated -- Mississippi Lime and Black River Lime. Significant differences in physical properties of these hydrates were observed. However, no relationship between the measured physical properties and the SO₂ reactivity was observed. Within the scope of this work, SO₂ reactivity is not a function of quicklime source.

When compared with commercial hydrates prepared from the same quicklime, the hydrates produced in the bench-scale unit showed significantly lower surface areas and SO₂ reactivities. As a result, the correlations developed in this study do not apply to commercial hydrates.

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ADVANCED IN-DUCT SORBENT INJECTION FOR SO₂ CONTROL,
DOE CONTRACT DE-AC22-91PC90360,
TOPICAL REPORT NO. 6, TASK 5: CONCEPTUAL COMMERCIAL PROCESS DESIGN
AND ECONOMIC EVALUATION

ABSTRACT

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For Task 4, Data Analysis and Computer Modeling, the objective was to develop two computer models. The first computer model would correlate sorbent properties with hydration parameters, while the second would correlate desulfurization performance with the sorbent properties. A two-level factorial program was undertaken to examine the effects of selected hydration process variables on some of the physical and chemical properties of the hydrates produced and on their SO₂ reactivity. A bench-scale hydrator was used to convert quicklime samples to hydrated limes under controlled processing conditions. Two quicklimes were hydrated -- Mississippi Lime and Black River Lime. Significant differences in physical properties of these hydrates were observed. However, no relationship between the measured physical properties and the SO₂ reactivity was observed. Within the scope of this work, SO₂ reactivity is not a function of quicklime source.

When compared with commercial hydrates prepared from the same quicklime, the hydrates produced in the bench-scale unit showed significantly lower surface areas and SO₂ reactivities. As a result, the correlations developed in this study do not apply to commercial hydrates.

ADVANCED IN-DUCT SORBENT INJECTION FOR SO₂ CONTROL,
DOE CONTRACT DE-AC22-91PC90360,
TOPICAL REPORT NO.5, TASK 4: DATA ANALYSIS AND COMPUTER MODELING

BACKGROUND AND INTRODUCTION

The objectives of the project entitled "Advanced In-Duct Sorbent Injection for SO₂ Control" (DOE Contract DE-AC22-91PC90360) are to improve the applicability of in-duct sorbent injection technology as a compliance option for the 1990 Clean Air Act Amendments and to reduce total SO₂ control costs. Specific desulfurization performance targets were to achieve 90% SO₂ removal and 60% sorbent utilization, while retaining the low capital cost and retrofit advantages inherent to in-duct technology. These targets represent a substantial improvement over existing sorbent injection technologies.

In Subtask 2.1 of this project, Evaluation of Advanced Concepts, pilot plant tests showed that a process concept, called the Advanced Coolside process, had the potential to achieve the process performance targets (Topical Report No. 1¹). SO₂ removals greater than 90% and sorbent utilization efficiencies greater than 60% were achieved. Other concepts for advanced sorbent injection were evaluated in Subtask 2.1, but none showed the potential to meet the process performance objectives. As recommended in the first topical report,¹ all further testing focused on optimizing the Advanced Coolside process.

The Advanced Coolside process, shown schematically in Figure 1, involves flue gas humidification to near the saturation point using a contacting device that simultaneously removes most of the fly ash from the flue gas. The sorbent (hydrated lime or hydrate) is injected into the highly humid flue gas downstream of the contactor, where it captures SO₂ before being removed by the existing particulate collector. Very high humidity allows high SO₂ removal. High sorbent utilization is achieved by sorbent recycle. Greater recycle ratios are possible than with existing in-duct sorbent injection processes because fly ash is removed by the contactor before sorbent injection. Furthermore, previous testing¹ showed that addition of some moisture to the recycle sorbent before reinjection can significantly improve process performance.

In Subtask 2.1 of this project, several approaches were identified for improving the Advanced Coolside process, including optimization of sorbent recycle, optimization of process equipment to reduce capital cost, and optimization of the sorbent.

Recycle optimization and process design optimization were evaluated through pilot plant tests in Subtask 2.2 and are reported in Topical Report No. 2.² By optimizing recycle, 90% SO₂ removal was achieved at sorbent utilizations of up to 75%, exceeding the original performance target of 60% sorbent utilization. Recycle tests showed that the Advanced Coolside process has the potential for very high SO₂ removal efficiency. With a baghouse, the Advanced Coolside process achieved removals of >99% with sorbent utilization efficiencies exceeding 60%. In the design optimization portion of this program a second generation contactor and a third generation contactor were designed, tested and optimized through pilot plant testing. For both designs, tests were conducted to maximize humidification efficiency while reducing flue gas pressure drop and water flow. Besides contactor optimization, the recycle sorbent wetting/mixing equipment was optimized. A pugmill was evaluated to replace the high intensity mixer used in initial recycle tests. Substitution of a pugmill results in significant capital and operating cost savings.

In the Sorbent Optimization program (Subtask 2.3), we explored means of improving performance and economics of the Advanced Coolside process through optimization of the sorbent system, as described in Topical Report No. 3.³ Pilot plant tests of commercial and specially prepared hydrated limes showed that the process is relatively insensitive to the source of the quicklime or hydrate. This is an important economic advantage, allowing the use of the lowest cost sorbent available at a site. Pilot plant tests showed that very small amounts of additives added to the sorbent within the Advanced Coolside process can marginally improve performance; however, additives are not necessary to exceed process performance targets. A pilot plant hydration study was conducted in cooperation with Dravo Lime Company. The results of that study provided the data for the modeling effort discussed in this report.

Information generated in Subtasks 2.1, 2.2, and 2.3 was used to optimize the Advanced Coolside process. The optimized process was the subject of additional

tests as reported in Topical Report No. 4,⁴ Task 3. Task 3 is divided into two subtasks: Performance Testing and Waste Characterization. The objective of Subtask 3.1, Performance Testing, was to generate performance and operability data for equipment design and scale-up of the process. Performance testing involved long-term pilot plant tests with continuous, 24 hours per day operation. For Subtask 3.2, Waste Characterization, the objective was to determine the chemical and physical properties of the waste materials to develop the data needed for designing waste handling and disposal systems for the process. The waste characterization test program was expanded to include exploratory tests of by-product utilization options. This involved pelletization tests and preliminary evaluation of the Advanced Coolside by-product for production of synthetic aggregate materials.

The objective of Task 4, Data Analysis and Computer Modeling, was to develop two computer models. This work is reported below. The objective of the first computer model was to correlate the chemical and physical properties of the sorbent with continuous hydration parameters. The second model was to correlate desulfurization performance with these physical properties. To this end, a pilot plant hydration study was undertaken in cooperation with Dravo Lime Company. Experimental results of this hydration study are presented in Topical Report No. 3.³ This report presents an in-depth analysis of these data using statistical computer modeling.

PROCEDURES

EXPERIMENTAL DESIGN

In cooperation with Dravo Lime Company, a test program was conducted to investigate the effects of hydration process variables on resulting hydrate properties and to investigate the effect of these hydrate properties on desulfurization performance. Two quicklimes were hydrated using the continuous, bench-scale lime hydration pilot plant at the Dravo Lime Company test facility. These hydrates were tested in the Advanced Coolside pilot plant to evaluate their SO₂ reactivity. Physical properties believed to affect SO₂ reactivity were measured by Dravo and by CONSOL.

A two-level factorial experimental program was designed in cooperation with the Dravo Lime Company. The hydration process variables studied were: feed quicklime particle size, water temperature, quicklime feed rate and excess water content of the hydrate. Excess water is the projected moisture content of the product hydrate calculated from the stoichiometric water requirements, evaporation losses and the water temperature. Quicklimes from two sources were examined in the study.

The boundary conditions selected for the hydration process variables covered the normal operating range of commercial hydrators. Process conditions were controlled at the boundary conditions of each variable and at an overall center point. The center point value was the average of the extremes. For a four-variable, two-level factorial design, this requires seventeen sets of experimental conditions. Table 1 lists the control points selected for each variable. Two different quicklimes, Mississippi Lime Company quicklime and Dravo Lime Company Black River quicklime, were selected as feed stocks. With four control variables, the seventeen sets of experimental conditions required consist of sixteen corner points and one center point. There was no replication of any point except the center point. After preliminary evaluation of the hydrated Mississippi quicklime, the quicklime feed rate was dropped from the experimental design since it appeared to affect the SO₂ removal the least. The resulting three-variable, two-level factorial test required eight sets of process conditions and one center point for the Black River quicklime. The control

points of the hydration process variables of the Mississippi and Black River quicklimes are listed in Tables 2 and 3, respectively.

After hydration, the products were analyzed for various physical properties. Porosity, BET surface area, hydrate particle size and product moisture content were measured for each hydrate. Reactivity of the hydrates to sulfur dioxide was determined by two different techniques: a laboratory-scale sorbent utilization test and Advanced Coolside pilot plant once-through SO₂ removal test. The methods used for these determinations are presented below.

HYDRATION

Dravo Hydration Pilot Plant Description

The Dravo Lime Company hydration bench-scale pilot plant is a continuous, horizontal hydrator having a production capacity of up to 3 ton per day. Quicklime is stored in 55-gallon drums and manually emptied into a feed hopper. From this hopper, the quicklime is delivered onto a variable speed conveyor. Quicklime feed size can be varied. Feed rates can be varied from 60 to 240 lb/hr. The conveyor delivers the quicklime into a mixing chamber equipped with interlocking, sectional screw flights, which counter-rotate to provide intimate mixing with the hydration water. The hydration water is delivered directly into the mixing chamber or sprayed onto the quicklime through a nozzle. Water temperatures, water addition rates and lime feed rates can be adjusted for production of specially formulated hydrates.

The steam produced by the heat from the hydration reaction is vented. The hydrating lime is impelled into a seasoner. In the seasoner, the hydration process continues to completion. The quicklime-hydrate-water mixture moves along the length of the seasoner propelled by a continuous screw conveyor equipped with thermocouples to monitor hydrate temperatures. An adjustable dam at the end of the seasoner controls residence time. The hydrated particles overflow the dam and are discharged into 55-gallon drums. The hydrate is not air classified. (Some commercial processes routinely perform air classification to separate the coarser, heavier particles.) Feeding and discharging occur continuously; that is, the unit operates continuously. The unit is designed so the hydration results can be scaled-up to a commercial sized unit.

Hydration Test Procedures

For the CONSOL test program, Dravo Lime Company produced hydrates by varying the lime source, quicklime feed size, quicklime feed rates, hydration water temperature, and by varying the excess water content in the final product. An on-site product moisture was determined and used to adjust the water feed to the hydrator to control the excess water in the final hydrate product.

SORBENT CHARACTERIZATION EQUIPMENT

Surface Area, Pore Volume and Porosity

These properties were measured using a Micromeritics DigiSorb 2600 nitrogen adsorption apparatus. This instrument measures the surface area and the pore size of materials based upon the physical adsorption of pure nitrogen gas at 77 K and pressures ranging from 2% to 99.8% of the N₂ saturation pressure (0.02 to 0.998 P/P₀). Surface areas were calculated, using the Brunauer, Emmett and Teller (BET) equation, from the volume of N₂ adsorbed at five relative pressures between 0.05 and 0.21 P/P₀ (five-point BET method). Pore volumes were calculated from the total volume adsorbed at P/P₀ = 0.985. Porosity was calculated using the following equation:

$$\text{Porosity} = \frac{P_v}{\frac{1}{D} + P_v} \quad (1)$$

where

P_v = pore volume, $\frac{\text{cm}^3}{\text{g}}$, and
 D = density of the solid.

A density of 2.24 g/cm³ was assumed for all the samples. Sample size was typically 1 g. The samples were vacuum degassed at 125 °C for 60 minutes prior to analysis. The weight lost during degassing was assumed to be free moisture. Surface area, pore volume, and porosity data are reported on a degassed weight basis.

Hydrate Particle Size

Hydrate particle size distribution and average particle size were measured using a Malvern Instruments 2600C EASY Particle Sizer M5.4 which determines particle size distribution in the range 1.9 to 188 μm using a laser light scattering/diffraction technique. The samples were dispersed in acetone immediately before analysis.

In addition, hydrate particle size analyses were conducted by Dravo Lime Company on hydrates produced in the hydration pilot plant.

Thermogravimetric Analysis (TGA)

The weight loss versus temperature data were collected using a Perkin Elmer 7-Series Thermogravimetric Analyzer. These data determine the degree of hydration. Samples were heated from 30 to 1000 °C at a rate of 25 °C/min. A continuous flow of dry nitrogen gas was maintained. Sample weight was typically 10 to 20 mg. The free moisture, calcium hydroxide, and calcium carbonate contents were determined based on the weight loss in three temperature ranges: 30 to 105 °C (free moisture), 350 to 525 °C (Ca(OH)_2 decomposition), 525 to 750 °C (CaCO_3 decomposition). The degree of hydration was determined by comparing the Ca(OH)_2 content with the total calcium content. The total calcium content was determined using EDTA titration, as described below.

Other Analyses

The moisture was determined by the weight loss after drying to constant weight at 115 °C. The total calcium content was determined by acid digestion followed by titration at a pH of 10 with ethylene diamine tetracetic acid (EDTA) with a calcine indicator endpoint. Carbonate content was calculated from the total carbon content determined using a LECO CHN-1000 analyzer.

LABORATORY-SCALE UTILIZATION UNIT

The sorbents were screened before testing in the pilot plant using a fixed-bed laboratory reactor (Figure 2). This unit measures the SO_2 utilization of a sorbent. Topical Report No. 3³ contains a description of this test unit and the operating procedure for this unit.

ADVANCED COOLSIDE PILOT PLANT

Description of Advanced Coolside Process

Figure 1 shows a schematic of the Advanced Coolside process. A key feature of the process is the injection of an SO_2 sorbent into a high-humidity flue gas stream with most fly ash removed. This near-saturation condition provides an enhanced environment for SO_2 capture. A detailed description of the process is contained in Topical Report No. 3.³

Description of the Pilot Plant

Figure 3 is a process sketch of the Advanced Coolside pilot plant. It is designed to simulate integrated Advanced Coolside operation with combined flue gas saturation and fly ash removal using a contactor with sorbent injection downstream of the contactor into the saturated flue gas. The pilot plant consists of the following systems: a flue gas generation system, a flue gas/water contactor, a spent slurry handling system, sorbent injection systems, a recycle sorbent/moisture addition system, the test duct section/reactor, a baghouse, and a flue gas analysis system. This unit is capable of simulating the flue gas conditions exiting the air heater of a coal-fired boiler. A detailed description of the Advanced Coolside pilot plant and its operating procedures is found in Topical Report No. 3.³

CORRELATION PROCEDURES

Correlation of Individual Properties

As mentioned, the experiment design followed the classic two-level factorial design. That is, each variable had two control levels, high (+) and low (-). A two-level factorial can determine the *main effect* of each variable and *interactions* of the variables in combination. Use of a center point permits an estimate of the *degree of curvature*. Replication of the center point, in the absence of control point replication, is necessary to provide an estimate of the experimental error.

A two-level factorial design with three variables requires nine trials, or tests, as illustrated below. Eight trials represent the control points at the boundary conditions for each variable, and the last trial, Trial 9, is the center point.

Trial	VARIABLE		
	X ₁	X ₂	X ₃
1	-	-	-
2	+	-	-
3	-	+	-
4	+	+	-
5	-	-	+
6	+	-	+
7	-	+	+
8	+	+	+
9	0	0	0

This produces the following computing table for the analysis of this factorial design. The heading of each column shows which variable (X_1), or interaction (X_1X_2) is associated with resulting effect.

Trial	Mean	X_1	X_2	X_1X_2	X_3	X_1X_3	X_2X_3	$X_1X_2X_3$
1	+	-	-	+	-	+	+	-
2	+	+	-	-	-	-	+	+
3	+	-	+	-	-	+	-	+
4	+	+	+	+	-	-	-	-
5	+	-	-	+	+	-	-	+
6	+	+	-	-	+	+	-	-
7	+	-	+	-	+	-	+	-
8	+	+	+	+	+	+	+	+

For each column, the following are calculated: sum of plus trials, sum of the minus trials, difference between these sums (plus - minus) and finally, the effect. The effect equals the difference divided by the number of plus signs in the column. This effect is must be larger than the minimum significant factor [MIN] to be included in the resulting correlation. [MIN] is calculated

$$[\text{MIN}] = t s \sqrt{\frac{2}{mk}} \quad (2)$$

where

t = the value of Student's t at the
desired probability level with
the number of degrees of freedom in s ,
 s = pooled standard deviation,
 m = number of + signs in the column (a constant), and
 k = number of replicates of each trial (one in this case) .

In the following discussion only the significant effects, that is, greater than the [MIN], are presented. None of the *degree of curvature* effects was significant.

Correlation of SO₂ Capture versus Sorbent Properties

Standard Least Squares techniques were used to evaluate the effects of the sorbent properties on sulfur capture and sorbent utilization. Results of this work will be discussed later.

CORRELATION AND MODELING OF EXPERIMENTAL RESULTS

CORRELATION OF INDIVIDUAL PROPERTIES

General Observations

Results of the sorbent characterization studies are tabulated in Table 4 for the hydrates of Mississippi lime and in Table 5 for those of Black River lime. Tables 6 and 7 list the respective desulfurization results.

As previously discussed, a standard two-level factorial experimental design was used in this study. Before examining the relationships predicted for the individual physical and chemical properties, a summary of the interrelationships is presented in this section. The surface area and single-pass desulfurization capacity of the hydrates produced by the continuous, bench-scale hydrator are lower than those produced by a commercial hydrator. Thus, details of this evaluation, specifically the final correlations, cannot not be applied directly to commercial hydrates or commercial processes.

Surface Area, Pore Volume, and Porosity. The surface areas, pore volumes and porosities were higher for the Mississippi hydrate than for the Black River hydrate. The surface areas of the hydrates of Mississippi quicklime ranged from 14.1 to 17.5 m²/g and the porosities ranged from 14.5 to 19% (Table 4). The surface areas of the sorbents made from Black River quicklime ranged from 11.8 to 15.3 m²/g and the porosities ranged from 10.6 to 14% (Table 5). Surface areas of the hydrates produced in the Dravo pilot plant were lower than the surface areas of a commercial hydrate produced from the same quicklime. Typical surface areas for commercial Mississippi hydrated lime are 22 to 24 m²/g, while typical surface areas for Dravo Black River hydrated lime are 14 to 15 m²/g.

Hydrate surface area was affected by the hydration process variables; however, the effects differed for the two different quicklimes. The BET surface area of the Mississippi hydrate correlated with the water temperature and quicklime feed rate. For the Black River hydrate, the BET surface area correlated with the excess water and quicklime feed size.

Sorbent porosity was higher at larger BET surface areas. However, the Mississippi hydrates had higher porosities than the Black River hydrates at

similar surface areas. This suggests that the average pore in the Mississippi hydrate was larger than in the Black River hydrate. Porosity was more dependent on the lime source than any controlled process variable.

The surface area and porosity analyses were duplicated for four of the Black River hydrate samples to determine the reproducibility of the analysis method. Results of the duplicated analyses are shown in Table 5. The results show that the reproducibility was $\pm 1.6 \text{ m}^2/\text{g}$ for surface area measurements and $\pm 0.3\%$ for porosity measurements at 95% confidence level. This is typical for surface area and porosity determinations using this instrument.

Hydrate Particle Size. The average particle sizes of the hydrates are shown in Tables 4 and 5. These data were measured by Dravo. The Mississippi hydrate particle size depended on the size of the feed quicklime. The quicklime feed with the larger particle size produced smaller hydrate particles -- opposite the expected effect. For Black River quicklime, the hydrate particle size was smaller than that of Mississippi hydrate. The size of the Black River hydrate was less influenced by the process variables. The dependence on the water temperature and on excess water was low.

Hydrate Product Moisture. The hydrate product moisture is the actual moisture content of the hydrate sample at the time it was tested at the Advanced Coolside pilot plant. Hydrate product moisture is affected by the excess water control point, as expected. Not expected was the dependence on the quicklime source. No other consistent relationship is evident.

Degree of Hydration. The degree of hydration determined by TGA ranged from 84 to 98% for the Mississippi lime hydrate and 86 to 93% for the Black River hydrate as shown in Tables 4 and 5. For both limes, the degree of hydration increased with excess water.

Other Physical Analyses. The hydrate moisture, calcium carbonate, calcium hydroxide and total calcium contents for the samples are shown in Tables 4 and 5.

Sorbent SO₂ Reactivity. For SO₂ removal in the Advanced Coolside process, lime source did not significantly affect the results. At the close approach to

saturation (highly humid) conditions present in this process, differences in sorbent properties were not statistically significant. The removals observed in these tests ranged from 30 to 60% for the duct and 62 to 78% for the system.

Correlations

The correlations derived from this study are discussed below. The coefficients of the correlation are calculated based on the assumption that the variables have values of -1, 0, or +1. The variable is at the lower control point (-1), center point (0) or the upper control point (+1). Thus, for the process variable water temperature of 160 °F substitute a value of -1 into the equation to obtain the effect. Similarly, substitute +1 for a water temperature of 200 °F or 0 for 180 °F.

BET Surface Area. The BET surface areas varied about 20% depending upon the quicklime source. The Mississippi lime hydrate surface area was higher than that of the Black River lime hydrate. In addition the functional relationships differ. For Mississippi lime hydrate, the correlation equation 3 is

$$SA_{ML} = 15.75 + 0.46 \times T_w + 0.92 \times L \quad (3)$$

T_w = Water Temperature

L = Lime Feed Rate

SA_{ML} = Surface Area of Mississippi Lime, m^2/g

The equation 4 for Black River lime hydrate is

$$SA_{BRL} = 13.1 + 0.45 \times D_{QL} + 0.50 \times W_{EX} + 0.34 \times D_{QL} \times W_{EX} + 0.34 \times D_{QL} \times T_w \times W_{EX} \quad (4)$$

SA_{BRL} = Surface Area of Black River lime, m^2/g

W_{EX} = Excess Water

D_{QL} = Particle Size of Quicklime

Plots of these correlations are shown in Figures 4 and 5. As discussed, the surface area depends also upon the quicklime source. The mean surface area of the Mississippi hydrate (15.75) is greater than the value calculated for the

Black River lime hydrate (13.11). This difference is significant at the 99% confidence level. There were no common links to control variables in equations 3 and 4.

Porosity. Plots of the correlations for the porosities for the hydrates of Mississippi lime and Black River lime are shown in Figures 6 and 7. For Mississippi lime hydrate, the correlation (5) is

$$P_{ML} = 16.4 + 0.79 \times L + 0.70 \times W_{EX} \quad (5)$$

P_{ML} = % Porosity of Hydrated Mississippi Lime

For Black River lime hydrate the correlation for porosity (6) is

$$P_{BRL} = 12.3 - 0.23 \times D_{QL} \times T_W + 0.80 \times W_{EX} + 0.38 \times D_{QL} \times W_{EX} + 0.37 \times D_{QL} \times T_W \times W_{EX} \quad (6)$$

P_{BRL} = % Porosity of Hydrated Black River Lime

While the center point value and functional relationship are again different for the hydrate porosities from these two quicklimes, the correlations share similar relationships with excess water. However, porosity was a more dependent on the quicklime source than any controlled process variable. The difference in the mean porosity values for the quicklime source is significant at the 99% confidence level. Thus, porosity is very dependent on source of the quicklime for the two quicklimes examined.

Hydrate Particle Size. The hydrate product size from the batch hydrator was measured on-site by Dravo. For Mississippi lime hydrate, the particle size depended on feed quicklime size. (See Figure 8.) The hydrate particle size correlation equation 7 is

$$D_{ML} = 7.7 - 2.9 \times D_{QL} \quad (7)$$

D_{ML} = Average Particle Diameter of Hydrated Mississippi lime, μm .

However, for the Black River lime hydrate, the hydrate particle size was much smaller and less influenced by the process variables. No dependence on quicklime feed size was evident. Instead, the Black River lime hydrate depended on the water temperature and excess water. For Black River lime, the equation 8 shown in Figure 9 is

$$D_{BRL} = 5.0 + 0.30 \times T_w - 0.35 \times W_{EX} \quad (8)$$

D_{BRL} = Average Particle Diameter of Hydrated Black River lime, μm

These correlations are completely different showing no common functionality. The mean values are statistically equivalent, but the standard deviation of the Mississippi lime hydrate particle sizes was very large. Statistically, hydrate particle size does not depend on the quicklime source. There does appear to be a fundamental difference for the quicklimes in the effect of hydration on the hydrate particle size. For Mississippi lime, the hydrate particle size varied from 3.6 to 18.1 μm , while the Black River hydrates only varied from 4.1 to 5.8 μm . This is reflected in the magnitude of the correlation coefficients as shown in equations 7 and 8.

Hydrate Product Moisture. The hydrate product moisture is a measured value. These measured product moistures were not the same as the set points of the excess water process variable. Of course, a strong relationship between the two is expected. The product moisture correlations versus the process variables are shown below. Not expected is that the product moisture is strong function of process variables other than excess moisture for both limes. These samples were collected at the time of testing in the Advanced Coolside pilot plant and the moisture determined by CONSOL. The correlation (9) for the moisture content of the Mississippi lime hydrate, as shown in Figure 10, is

$$W_{ML} = 2.7 + 0.34 \times L + 0.40 \times W_{EX} \quad (9)$$

W_{ML} = Water Content of Hydrated Mississippi lime, wt %

The predicted relationship (10) for Black River lime hydrate (See Figure 11.) is

$$W_{BRL} = 1.9 + 0.65 \times T_W + 0.78 \times W_{EX} \quad (10)$$

The difference between the mean hydrate product moistures of the two quicklimes is significant at the 90% confidence level. These hydrates show similar dependencies on excess water with the hydrate product moisture increasing as excess water increases.

Degree of Hydration. As expected, the degree of hydration is a function of excess water. For Mississippi lime, the correlation (11) is

$$H_{ML} = 92 + 2.2 \times W_{EX} \quad (11)$$

H_{ML} = Degree of Hydration for Mississippi Lime, %

This is shown in Figure 12. Figure 13 shows the relationship for Black River lime. This correlation (12) is

$$H_{BRL} = 90 + 1.6 \times W_{EX} \quad (12)$$

H_{BRL} = Degree of Hydration for Black River Lime, %

The correlation constants for equations 11 and 12 are not statistically different.

Reactivity to Sulfur Dioxide. The SO_2 reactivity of the hydrates was determined in two ways. A calcium utilization was measured in CONSOL's laboratory-scale reactor, and duct and system SO_2 removals were measured by once-through tests in the Advanced Coolside pilot plant. Tables 6 and 7 list the SO_2 reactivities measured in the laboratory-scale and pilot plant-scale units. Details of the run conditions may be found in Topical Report No. 3.

For the reactivities measured in the pilot plant, no significant difference in SO_2 removal was attributable to quicklime source. Further studies are required

to extend this finding to other sorbents. However, previous studies of selected commercial hydrates³ indicated that sorbent source was not an important consideration at Advanced Coolside process conditions.

SO₂ reactivities of the hydrates produced in this pilot plant study were much lower than those of commercial hydrates. As reported in Topical Report No. 3,³ commercial hydrates showed duct removals of 51 to 54% and system removals of 72 to 80%. Of the 31 pilot plant-hydrates examined in this study, only two -- one from each quicklime -- showed removals in these ranges. Most of the others were in the 30-45% range for the duct and 60-70% range for the system. The bench-scale hydrator does not appear to produce as active a sorbent as the commercial hydrator. As a result, the correlations discussed below are not directly applicable to commercial hydrates.

Laboratory-Scale Sorbent Utilization. The behavior of Mississippi lime hydrate during laboratory-scale sorbent utilization testing was not significantly dependent on any process variable. Of the three hydrates produced at center-point experimental conditions, two had nearly the highest sorbent utilizations and one the lowest. As a result, statistic analysis was inconclusive.

For the Black River lime hydrate, the quicklime feed size and product moisture influenced the sorbent utilization. The quicklime feed size and water temperature cross product also influenced sorbent utilization. (See Figure 14.) The resulting equation 13 was

$$\begin{aligned} \text{Laboratory-Scale Utilization}_{\text{BRL}}, \% &= 49 + 3.2 \times D_{\text{QL}} \\ &\quad - 3.0 \times D_{\text{QL}} \times T_{\text{W}} \\ &\quad - 2.2 \times W_{\text{EX}} \end{aligned} \quad (13)$$

Advanced Coolside SO₂ Removal, Duct. The duct SO₂ removal in Advanced Coolside pilot plant tests correlated with the quicklime feed size and the excess water for both Black River and Mississippi quicklimes. However, the effect of

quicklime size was opposite for the two different quicklimes, as shown by the equations below. For the Mississippi lime this correlation (equation 14) is

$$\Delta \text{SO}_2 (\text{ID})_{\text{ML}} = 40 + 3.8 \times D_{\text{QL}} + 4.4 \times W_{\text{EX}} \quad (14)$$

$\Delta \text{SO}_2 (\text{ID})_{\text{ML}}$ = In-duct SO_2 removal with Mississippi Lime, %

For Black River Lime the correlation (15) is

$$\Delta \text{SO}_2 (\text{ID})_{\text{BRL}} = 45 - 1.9 \times D_{\text{QL}} + 2.3 \times W_{\text{EX}} \quad (15)$$

$\Delta \text{SO}_2 (\text{ID})_{\text{ML}}$ = In-duct SO_2 removal with Black River Lime, %

These correlations are shown in Figures 15 and 16. Statistically, duct SO_2 removal was not affected by quicklime source. That is, the mean duct removals predicted by equations 14 and 15 are not significantly different. Both equations show a positive effect of excess water.

Advanced Coolside SO_2 Removal, System. The system SO_2 removal was affected by the quicklime feed size and excess water for the hydrates of both quicklimes. These variables had a major influence on the removal behavior in the system. The magnitudes and effects were similar to those observed in the case of duct SO_2 removals. This is illustrated in Figure 17 for the Mississippi lime hydrate. The correlation (16) for Mississippi lime hydrate is

$$\Delta \text{SO}_2 (\text{S})_{\text{ML}} = 69 + 3.3 \times D_{\text{QL}} + 2.6 \times W_{\text{EX}} - 0.92 \times D_{\text{QL}} \times T_{\text{W}} \times W_{\text{EX}} \quad (16)$$

$\Delta \text{SO}_2 (\text{S})_{\text{ML}}$ = System SO_2 removal with Mississippi Lime, %

The Black River lime hydrate system SO_2 removal correlation (17) as shown in Figure 18 is

$$\begin{aligned}
\Delta \text{SO}_2 (S)_{\text{BRL}} = & 67 - 2.1 \times D_{\text{QL}} \\
& + 1.1 \times D_{\text{QL}} \times T_{\text{W}} \\
& + 3.7 \times W_{\text{EX}} \\
& - 2.2 \times D_{\text{QL}} \times W_{\text{EX}}
\end{aligned}
\tag{17}$$

$\Delta \text{SO}_2 (S)_{\text{HL}}$ = System SO_2 removal with Black River Lime, %

From previous investigations in the Advanced Coolside pilot plant, increases in the moisture content of the sorbent were expected to produce increased removal. However, the effect of feed quicklime feed size to the hydrator on SO_2 pickup was the opposite for the two sorbents. This behavior is similar to that exhibited in the duct. Comparing equations 14 with 16 and 15 with 17, the coefficient of the lime size is 3.3 for the Mississippi lime data set and -2.1 for the Black River Lime set. Thus, a difference for lime source on the effect of lime size. More research is required to ascertain the reason for this effect.

The mean SO_2 removals in the system were not dependent on the lime source. The mean removals predicted by equations 16 and 17 are the same statistically. Thus, both the duct and the system SO_2 removals were independent of the quicklime source.

CORRELATION OF SORBENT PROPERTIES

The following discusses the relationships between the sorbent physical properties, and between SO_2 capture/calcium utilization and the sorbent physical properties. The physical properties discussed below are not the same as the control values discussed in the previous section. The Least Squares Method was used to develop the correlations. Standard statistical analysis was applied to examining the significance of population means, and the correlation coefficients. The final relationships are discussed below. Due, in part to the limited range of physical properties exhibited by these hydrates, no significant dependence of SO_2 capture on the physical properties of the hydrates was observed.

Surface Area-Porosity Relationships

Hydrate porosity was a function of BET surface area and quicklime source. This is shown in Figure 19. The hydrates of Mississippi lime and of Black River lime display a linear correlation between porosity and surface area. This

relationship is expected for these two physical properties. Separate relationships were found for each quicklime. A significant difference exists between the relationships predicted for the hydrates of Mississippi lime and of Black River lime. A Mississippi lime hydrate is more porous than the corresponding Black River lime hydrate. However, the slopes of hydrate porosity versus BET surface area curves are statistically identical. For a given surface area, the Mississippi lime hydrate has a higher porosity by an absolute 2% above that predicted for Black River lime hydrate.

SO₂ Reactivity Relationships

For these hydrates, pilot plant SO₂ removals in the system and the duct and laboratory-scale calcium utilizations were not dependent on BET surface area, porosity or moisture content. SO₂ removals also were not affected by the extent of hydration. The calcium utilization for the hydrates of Mississippi lime were affected by the extent of hydration, but those of Black River lime were not. However, these SO₂ removals and sorbent utilizations were much lower than those measured for commercial hydrates.³ As a result, these findings should not be extended to other process or commercial sorbents.

SO₂ removal was expected to be a function of BET surface area, porosity and moisture content. This is based upon the observations from conventional in-duct sorbent injection technologies. However, this was not the case for these hydrates. This may be a result of several factors. First, the variability of the physical properties of the hydrates produced in this study was small. Second, with this small change in physical properties, the inherent errors in determining SO₂ removals for the Advanced Coolside pilot plant may mask a small trend. The factorial experimental design that served as the basis for this data may mask the interrelationships. That is, the process control variables may interfere with effects from the physical properties. Finally, the Advanced Coolside process may be insensitive to small changes in the physical properties of the sorbent. Because of the large influence of the highly humid flue gas conditions, the effect of differences in porosity or surface area on the reactivity may be minor.

Duct and system SO₂ removals (Figure 20) and Ca utilizations (Figure 21) show no dependency on the BET surface areas. Hydrate porosity did not affect the SO₂

reactivity as shown in Figures 22 and 23. The SO_2 reactivity also was independent of the moisture content of the hydrates (Figures 24 and 25). This latter finding appears to contrast with the dependence displayed in equations 15, 16, 17, and 18. However, the effect of actual moisture content may be masked by other, unknown effects. As a result of these findings, it is not possible to model sorbent reactivity versus these hydrate physical properties. No statistically significant effect was found for BET surface area, porosity, hydrate moisture content or the source of the quicklime.

The extent of hydration did not affect the sorbent behavior in the pilot plant. See Figure 26 for duct and system SO_2 removals. The laboratory-scale utilizations for Black River lime hydrates were independent of the extent of hydration, while those for the hydrates from Mississippi lime were not. See Figure 27 for sorbent utilizations. For the SO_2 removals, the calcium utilizations might be low enough not to be affected by the unhydrated core. Similar behavior might account for the independence of the hydrates of the Black River lime. However, the reasons are not clear at this time.

CONCLUSIONS

The two-level factorial experimental program utilized in this study provided information on the effects of selected process control variables on hydration processes. Unfortunately, the bench-scale hydration pilot plant does not produce the same quality of hydrate available from a commercial-scale unit. Thus, while the conclusions are believed to be valid, the actual correlations developed in this study should not be applied to commercial hydrates.

For the physical properties of the hydrates examined in this program, there is little similarity between the correlations developed for the two quicklimes. The quicklimes are affected differently by the hydration process variables. In part, this may be due to actual differences in the quicklime feed or in the way the quicklime reacts to the hydration process.

These observations extend to the reactivity of the Ca(OH)_2 with SO_2 . While mean values of duct and system SO_2 removals were identical, the effect of quicklime feed size is the opposite for the two quicklimes evaluated in the study.

Reactivity of the hydrates was not a function of the physical properties examined in this study. BET surface area, porosity, hydrate moisture content and extent of hydration did not affect the reactivity. The reactivity was independent of sorbent source. However, the range of physical properties exhibited by these hydrate samples was narrow. This may account for these observation.

No single hydrated lime physical property dominates the SO_2 reactivity. The relationship is too complex for a simple approach. The most important properties affecting SO_2 reactivity in the Advanced Coolside process are either not governed by the hydration process or are a complex relationship between the physical characteristics determined above. The source of the quicklime did not affect the reactivity, at least for the Mississippi lime and the Black River lime used in this study. A previous study³ showed similar results. This finding is an important economic advantage for the Advanced Coolside process. Transportation accounts for as much as 20% of the sorbent cost. Using a local quicklime or hydrate would improve the process economics significantly.

ACKNOWLEDGMENT

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REFERENCES

1. Stouffer, M. R.; Withum, J. A.; Rosenhoover, W. A. "Advanced In-Duct Sorbent Injection For SO₂ Control, Topical Report No. 1, Task 2.1: Evaluation of Advanced Concepts", DOE/PC 90360-1, DOE Contract No. DE-AC22-91PC90360, September 1992.
2. Stouffer, M. R.; Withum, J. A.; Rosenhoover, W. A. "Advanced In-Duct Sorbent Injection For SO₂ Control, Topical Report No. 2, Subtask 2.2: Design Optimization". DOE/PC 90360-44, DOE Contract No. DE-AC22-91PC90360, November 1994.
3. Rosenhoover, W. A.; Maskew, J. T.; Withum, J. A.; Stouffer, M. R. "Advanced In-Duct Sorbent Injection For SO₂ Control, Topical Report No. 3, Subtask 2.3: Sorbent Optimization". DOE/PC 90360-42, DOE Contract No. DE-AC22-91PC90360, November 1994.
4. Wu, M. M.; Rosenhoover, W. A.; Stouffer, M. R.; Maskew, J. T.; Withum, J. A.; Winschel, R. A. "Advanced In-Duct Sorbent Injection For SO₂ Control, Topical Report No. 4, Task 3: Optimized Advanced Process Evaluation", DOE/PC 90360-46, DOE Contract No. DE-AC22-91PC90360, November 1994.

TABLE 1

PROCESS VARIABLES EXAMINED IN THE BENCH-SCALE HYDRATION PROGRAM

Process Variables	Variable Control Point		
	(-) Lower	(+) Upper	(0) Center
Feed Lime Size	1/8"x3/4"	3/4"x1 1/2"	1/8"x1 1/2"
Water Temperature, °F	160	200	180
Lime Feed Rate, lb/min	1.3	2.7	2.0
Excess Water, wt %	0.1 - 0.5	1.5 - 2.0	1.0 - 1.5

TABLE 2

MISSISSIPPI LIME HYDRATED IN DRAVO PILOT PLANT, HYDRATION CONDITIONS

Dravo Sample No.	Trial	Process Conditions							
		Two-Level Factorial Codes				Actual Variable Value			
		Feed Lime Size	Water Temp	Lime Feed Rate	Excess Water	Feed Lime Size, in.	Water Temp, °F	Lime Feed Rate, lb/hr	Initial Moisture, wt %
23	1	-	-	-	-	1/8 x 3/4	160	1.3	0.28
20	2	+	-	-	-	3/4 x 1 1/2	160	1.3	0.32
21	3	-	+	-	-	1/8 x 3/4	200	1.3	0.10
33	4	+	+	-	-	3/4 x 1 1/2	200	1.3	0.56
35	5	-	-	+	-	1/8 x 3/4	160	2.7	0.42
34	6	+	-	+	-	3/4 x 1 1/2	160	2.7	0.34
26	8	+	+	+	-	3/4 x 1 1/2	200	2.7	0.28
29	9	-	-	-	+	1/8 x 3/4	160	1.3	1.82
30	10	+	+	-	+	3/4 x 1 1/2	160	1.3	1.70
27	11	+	-	-	+	1/8 x 3/4	200	1.3	1.20
36	12	-	+	-	+	3/4 x 1 1/2	200	1.3	1.40
22	13	-	-	+	+	1/8 x 3/4	160	2.7	0.89
31	14	+	-	+	+	3/4 x 1 1/2	160	2.7	1.68
24	15	-	+	+	+	1/8 x 3/4	200	2.7	2.42
25	16	+	+	+	+	3/4 x 1 1/2	200	2.7	1.10
19	17a	0	0	0	0	1/8 x 1 1/2	180	2.0	0.54
37	17b	0	0	0	0	1/8 x 1 1/2	180	2.0	0.34
28	17c	0	0	0	0	1/8 x 1 1/2	200	2.0	1.17

TABLE 3
BLACK RIVER LIME HYDRATED IN DRAVO PILOT PLANT
HYDRATION CONDITIONS

Dravo Sample No.	Trial	Process Conditions					
		Two-Level Factorial Codes			Actual Variable Value		
		Feed Lime Size	Water Temp	Excess Water	Feed Lime Size, in.	Water Temp, °F	Initial Moisture, wt %
41	1	-	-	-	1/8 x 3/4	160	0.35
40	2	+	-	-	3/4 x 1 1/2	160	0.35
47	3	-	+	-	1/8 x 3/4	200	0.46
45	4	+	+	-	3/4 x 1 1/2	200	0.32
43	5	-	-	+	1/8 x 3/4	160	1.96
44	6	+	+	+	3/4 x 1 1/2	200	1.36
48	7	+	-	+	3/4 x 1 1/2	160	1.44
49	8	-	+	+	1/8 x 3/4	200	1.54
39	9a	0	0	0	1/8 x 1 1/2	180	0.61
42	9b	0	0	0	1/8 x 1 1/2	180	0.56
46	9c	0	0	0	1/8 x 1 1/2	180	0.77
50	9d	0	0	0	1/8 x 1 1/2	180	0.74

TABLE 4
CHARACTERIZATION OF SORBENTS MADE BY HYDRATION OF MISSISSIPPI QUICKLIME
IN THE DRAVO BENCH-SCALE HYDRATOR.

Dravo Test No.	Prod. H ₂ O, wt %	Surface Area, m ² /g	Pore Volume, cm ³ /g	Porosity, %	Average Particle Size, μm	CaCO ₃ , wt %	Degree of Hydration, %	Ca(OH) ₂ , wt %	Total Ca, wt %
23	2.0	15.3	0.080	15.3	18.1	2.5	90	88.0	52.8
20	2.4	14.4	0.076	14.5	5.6	3.3	84	82.8	53.1
21	2.1	14.5	0.077	14.6	13.9	4.6	90	87.7	52.7
33	1.9	16.0	0.085	16.0	3.8	2.5	95	92.8	52.9
35	2.4	16.8	0.088	16.4	6.6	3.1	92	90.3	53.3
34	3.0	15.2	0.083	15.7	3.6	4.4	92	90.1	52.9
26	2.5	17.3	0.089	16.6	-	2.6	91	89.7	53.2
29	3.2	14.3	0.086	16.2	5.3	3.6	94	91.5	52.8
30	3.3	14.2	0.086	16.1	3.8	3.6	95	91.9	52.2
27	2.0	16.3	0.089	16.7	-	1.7	95	92.5	52.7
36	2.3	14.1	0.081	15.4	6.4	3.4	95	92.3	52.3
22	3.0	16.4	0.095	17.6	15.3	0.8	94	92.3	53.1
31	3.5	16.1	0.102	18.5	4.4	3.2	96	91.9	51.7
24	4.7	17.5	0.103	18.8	5.9	4.4	98	93.6	51.6
25	3.1	16.5	0.094	17.4	-	3.9	94	90.5	52.2
19	2.3	14.1	0.078	14.9	13.0	3.1	90	87.8	53.0
37	2.7	16.5	0.091	16.9	4.2	2.9	94	92.5	53.0
28	2.8	15.2	0.090	16.8	5.2	2.0	96	92.4	52.2

TABLE 5

CHARACTERIZATION OF SORBENTS MADE BY HYDRATION OF BLACK RIVER QUICKLIME
IN THE DRAVO BENCH-SCALE HYDRATOR

Dravo Test No.	Prod. H ₂ O, wt %	Surface Area, m ² /g	Pore Volume, cm ³ /g	Porosity, %	Average Particle Size, μ m	CaCO ₃ , wt %	Degree of Hydration, %	Ca(OH) ₂ , wt %	Total Ca, wt %
41	1.1	11.8	0.057	11.2	5.6	1.7	90	86.6	52.0
40	0.4	13.1	0.060	11.8	4.1	2.0	91	87.4	51.7
47	2.8	13.3	0.063	12.4	5.7	1.1	90	86.2	52.0
45	0.1	12.3	0.053	10.6	5.8	2.2	86	82.2	51.8
43	2.1	13.0/ 12.9	0.065	12.8/ 13.3	4.4	1.5	91	85.7	50.9
44	4.2	14.4	0.071	13.8	4.5	1.9	94	88.2	50.9
48	1.3	14.4	0.069	13.3	4.5	2.5	93	87.5	50.7
49	3.0	12.7	0.065	12.6	5.0	2.1	92	87.2	51.4
39	2.6	14.4/ 13.7	0.068	13.2/ 13.2	4.8	2.1	91	86.4	51.5
42	1.1	14.3	0.067	13.0	5.7	2.3	88	84.3	51.5
46	2.8	15.2/ 15.1	0.071	13.8/ 13.7	5.2	2.3	92	88.2	51.9
50	2.6	15.3/ 13.9	0.069	13.3/ 13.4	5.6	1.6	92	87.9	51.7

TABLE 6

**MISSISSIPPI LIME HYDRATED IN DRAVO PILOT PLANT
DESULFURIZATION RESULTS**

Dravo Sample No.	Desulfurization Results		
	Laboratory Unit, Ca Utilization	Pilot Plant	
		Duct Removal, %	System Removal, %
23	61	34	64
20	42	46	69
21	48	33	62
33	62	38	70
35	58	30	62
34	66	38	69
26	43	39	71
29	61	42	67
30	69	43	75
27	55	34	68
36	51	49	70
22	58	45	69
31	65	60	78
24	67	44	70
25	47	42	75
19	43	39	67
37	68	35	67
28	64	36	69
Avg. of Cp =	58	36	68
Std. Dev. of CP =	13	1.8	1.0

TABLE 7

**BLACK RIVER LIME HYDRATED IN DRAVO PILOT PLANT
DESULFURIZATION RESULTS**

Dravo Sample No.	Desulfurization Results		
	Laboratory Unit Ca Utilization	Pilot Plant	
		Duct Removal, %	System Removal, %
41	43	45	63
40	57	40	63
47	44	44	64
45	52	43	64
43	46	51	78
44	46	46	68
48	57	44	65
49	53	49	73
39	43	43	65
42	50	42	65
46	46	45	68
50	47	41	66
Avg. of CPs =	47	43	66
Std. Dev. of CP =	3	1.8	1.4

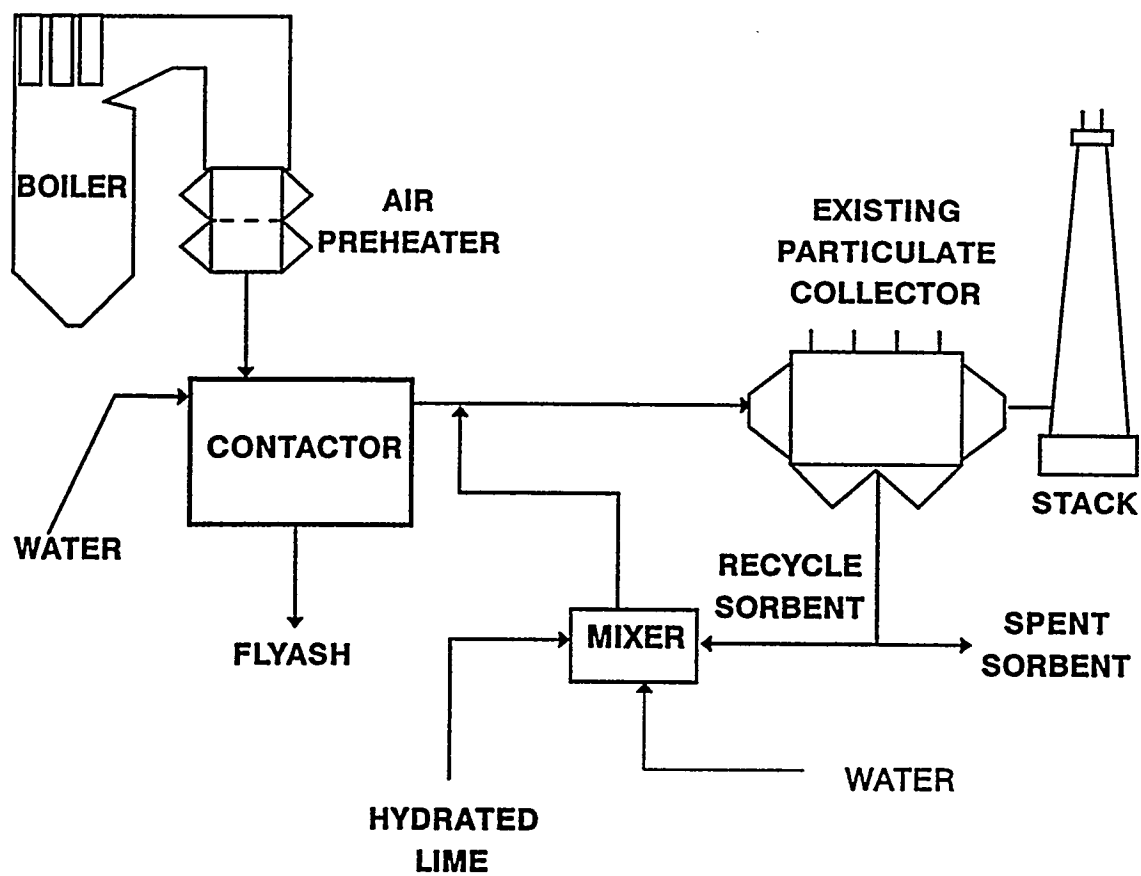


Figure 1. Schematic of Advanced Coolside Process.

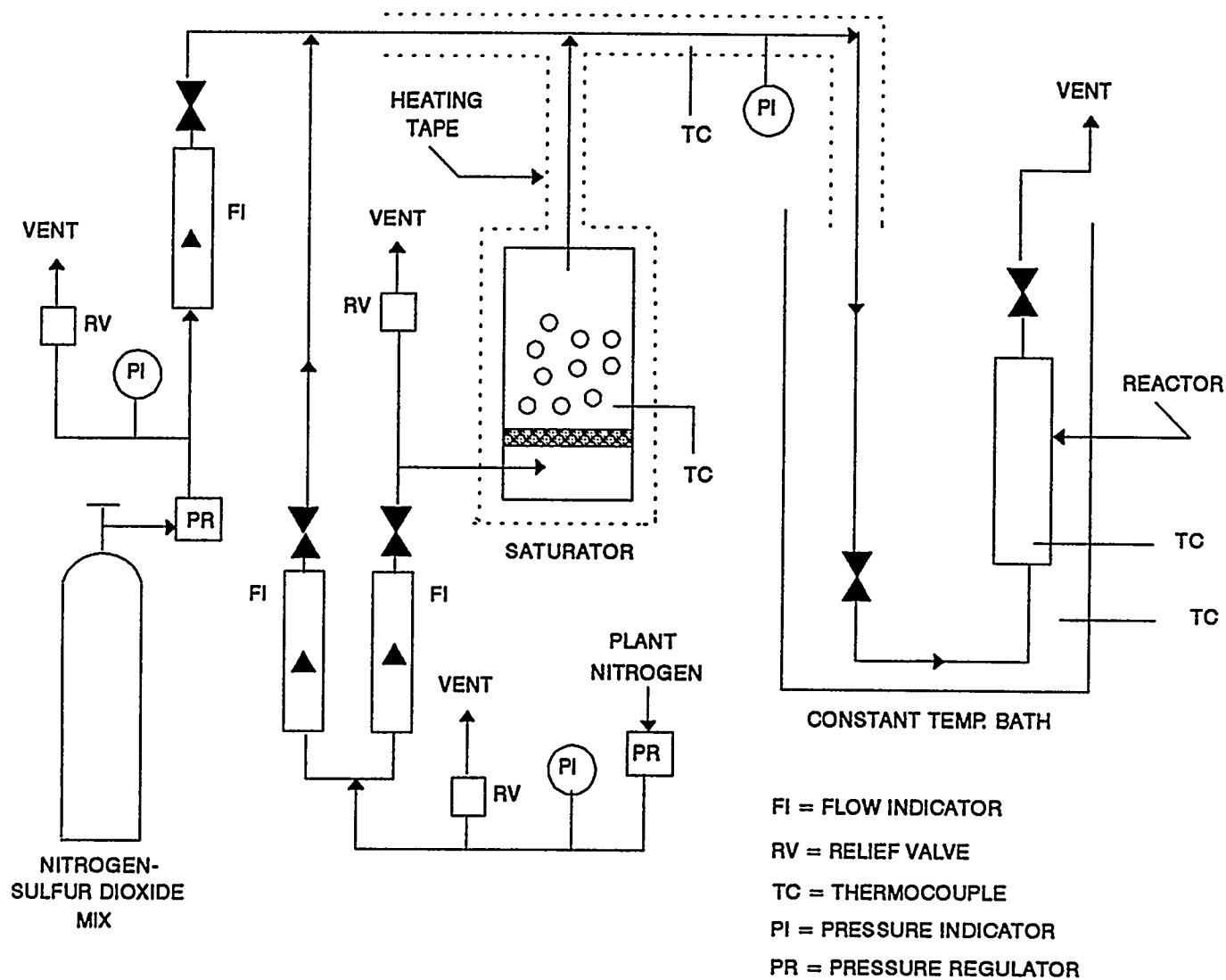


Figure 2. Sketch of Laboratory Fixed-Bed Reactor.

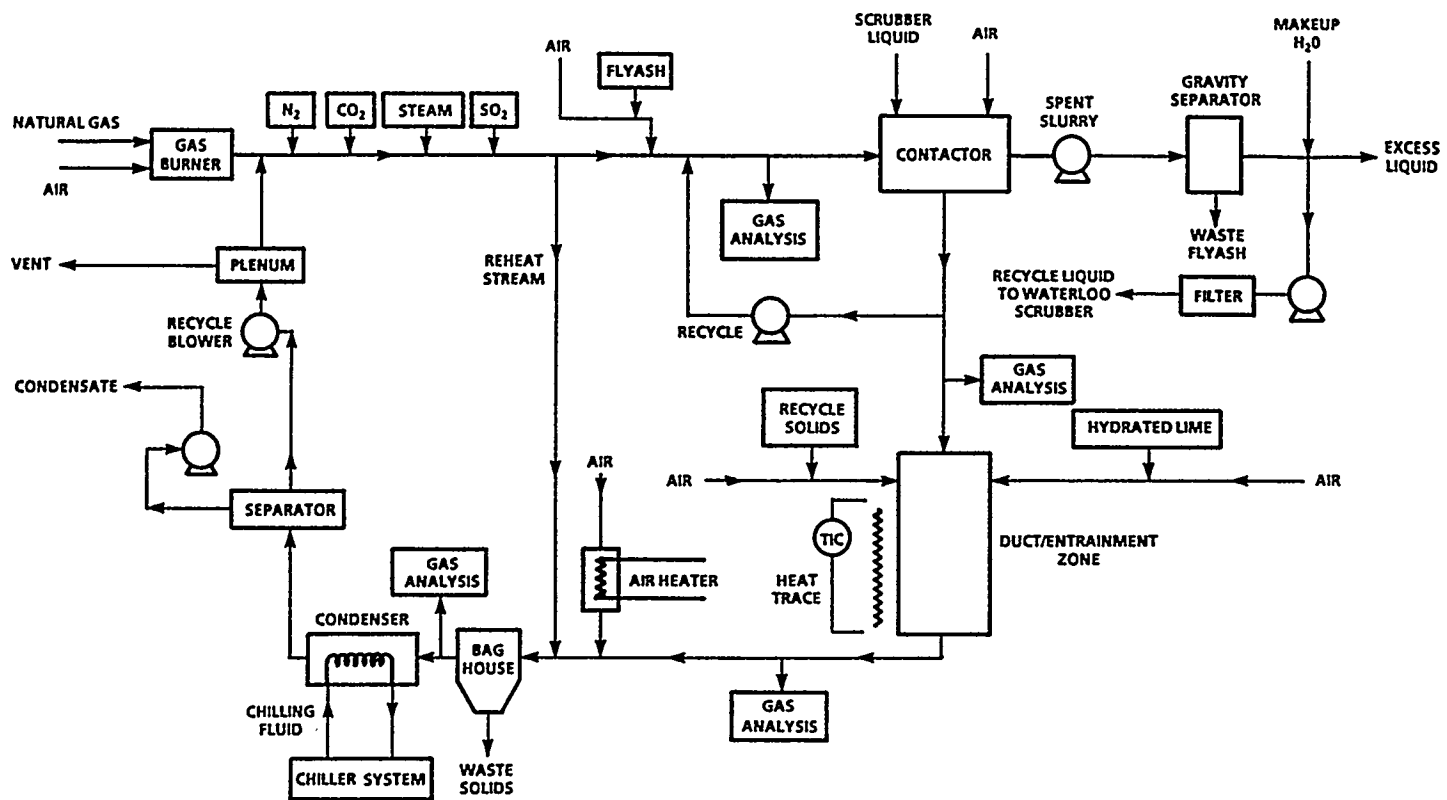
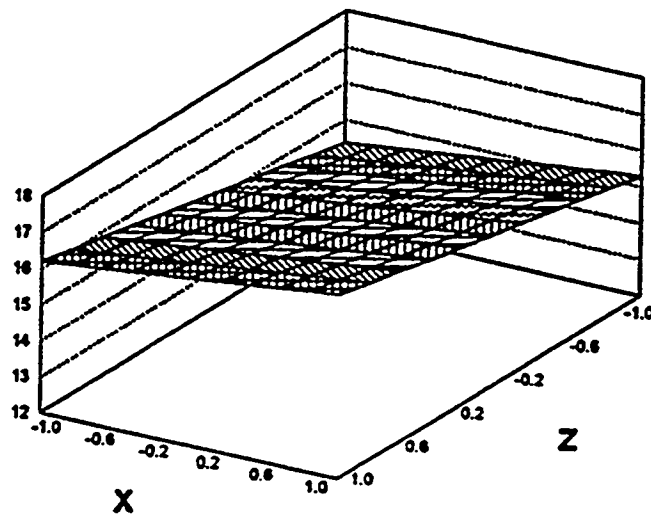


Figure 3. Schematic of Advanced Coolside Pilot Plant.



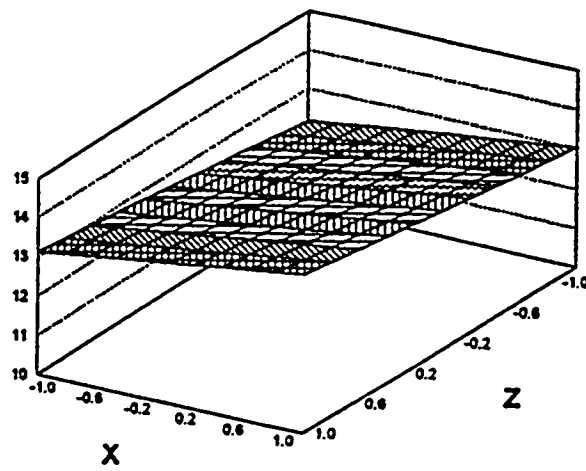
**Corner Values
(X, Z)**

(1,1)	= 17.1
(1,-1)	= 15.3
(-1,-1)	= 14.4
(-1,1)	= 16.2

Plotted Versus Water Temperature (X) and Lime Feed Rate (Z)

Figure 4. BET Surface Area for Mississippi Lime Hydrates.

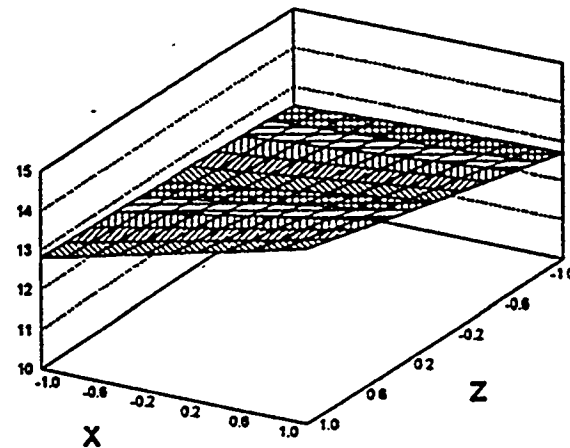
$$SA_{HL} = 15.8 + 0.46 \times T_w + 0.92 \times L$$



**Corner Values
(X, Z)**

(1,1) = 14.1
(1,-1) = 13.0
(-1,-1) = 12.2
(-1,1) = 13.1

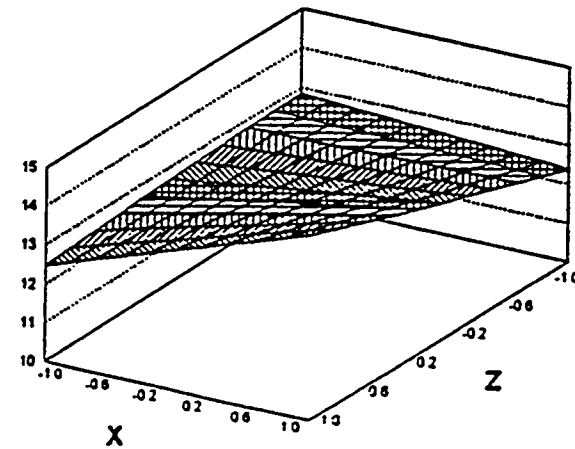
Plotted vs Lime Size (X) and Product Moisture (Z)
Water Temperature (-1), Held Constant



**Corner Values
(X, Z)**

(1,1) = 14.4
(1,-1) = 12.7
(-1,-1) = 12.5
(-1,1) = 12.8

Plotted vs Lime Size (X) and Product Moisture (Z)
Water Temperature (0), Held Constant



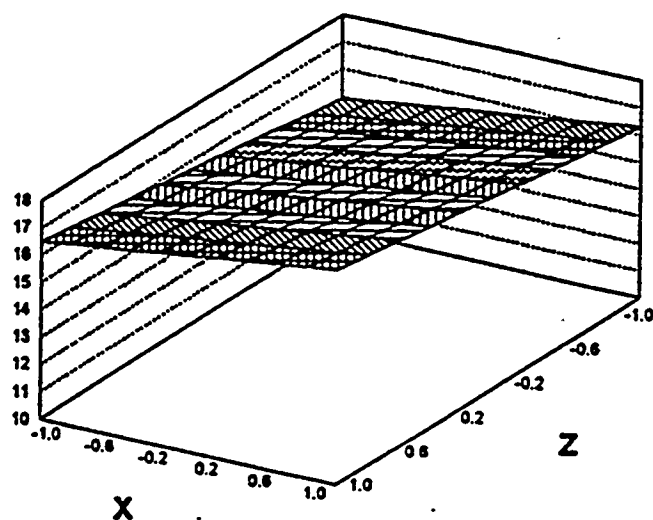
**Corner Values
(X, Z)**

(1,1) = 14.7
(1,-1) = 12.4
(-1,-1) = 12.8
(-1,1) = 12.5

Plotted vs Lime Size (X) and Product Moisture (Z)
Water Temperature (1), Held Constant

Figure 5. BET Surface Area for Black River Lime Hydrates.

$$\begin{aligned}
 SA_{BRL} = & 13.1 + 0.45 \times D_{QL} \\
 & + 0.50 \times W_{EX} \\
 & + 0.35 \times D_{QL} \times W_{EX} \\
 & + 0.35 \times D_{QL} \times T_W \times W_{EX}
 \end{aligned}$$



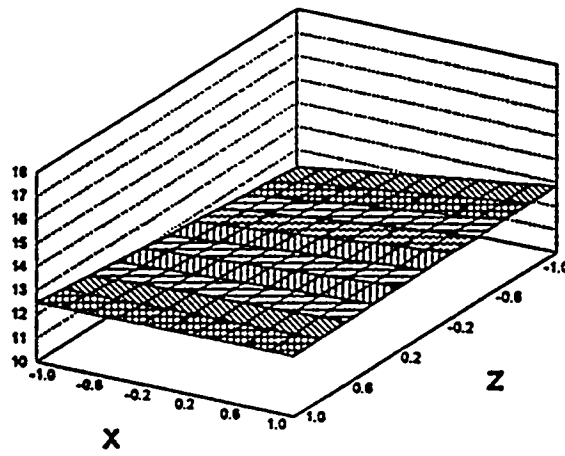
Corner Values
(X, Z)

(1,1)	= 17.9
(1,-1)	= 16.3
(-1,-1)	= 14.9
(-1,1)	= 16.5

Plotted Versus Product Moisture (X) and Lime Feed Rate (Z)

Figure 6. Hydrate Porosity for Mississippi Lime Hydrates.

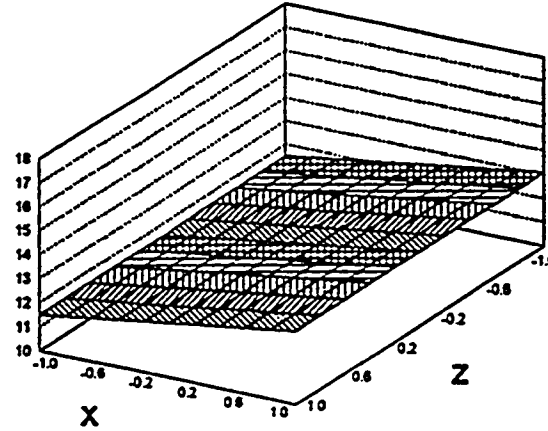
$$\begin{aligned}
 P_{ML} &= 16.4 \\
 &+ 0.79 \times L \\
 &+ 0.70 \times W_{EX}
 \end{aligned}$$



Corner Values
(X, Z)

(1,1) = 12.6
(1,-1) = 12.8
(-1,-1) = 11.3
(-1,1) = 12.5

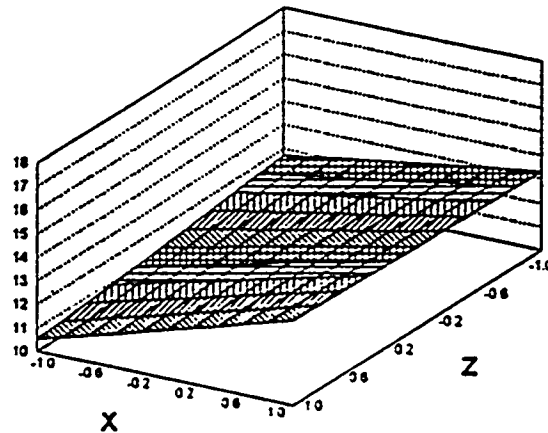
Plotted vs Product Moisture (X) and Water Temperature (Z)
Lime Size (-1), Held Constant



Corner Values
(X, Z)

(1,1) = 13.1
(1,-1) = 13.1
(-1,-1) = 11.5
(-1,1) = 11.5

Plotted vs Product Moisture (X) and Water Temperature (Z)
Lime Size (0), Held Constant



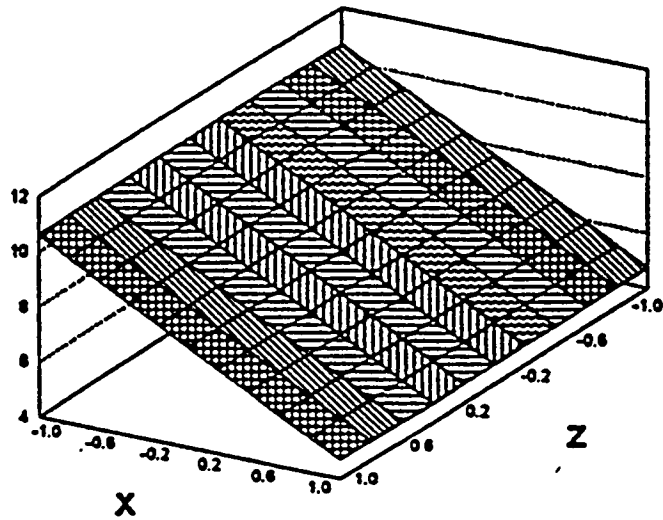
Corner Values
(X, Z)

(1,1) = 13.6
(1,-1) = 13.3
(-1,-1) = 11.7
(-1,1) = 10.5

Plotted vs Product Moisture (X) and Water Temperature (Z)
Lime Size (1), Held Constant

Figure 7. BET Surface Area for Black River Lime Hydrates.

$$P_{BRL} = 12.3 - 0.23 \times D_{QL} \times T_W \\ + 0.80 \times W_{EX} \\ + 0.38 \times D_{QL} \times W_{EX} \\ + 0.37 \times D_{QL} \times T_W \times W_{EX}$$

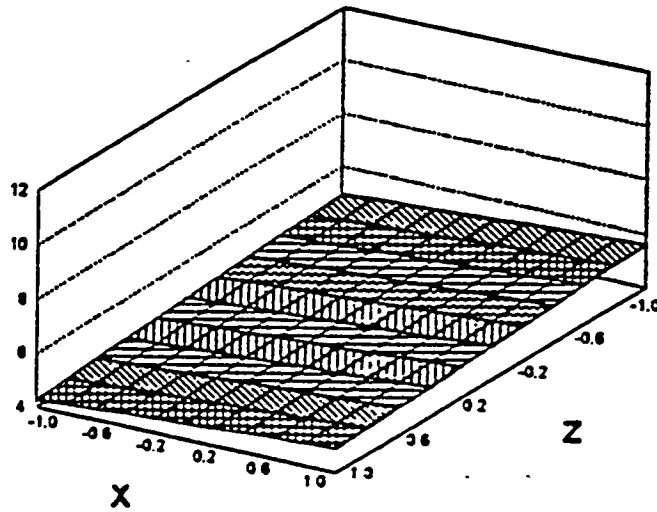


Corner Values
(X, Z)

(1,1)	= 4.7
(1,-1)	= 4.7
(-1,-1)	= 10.6
(-1,1)	= 10.6

Plotted vs Lime Size (X)

Figure 8. Particle Size for Mississippi Lime Hydrates.
 $D_{ML} = 7.7 - 2.9 \times D_{QL}$

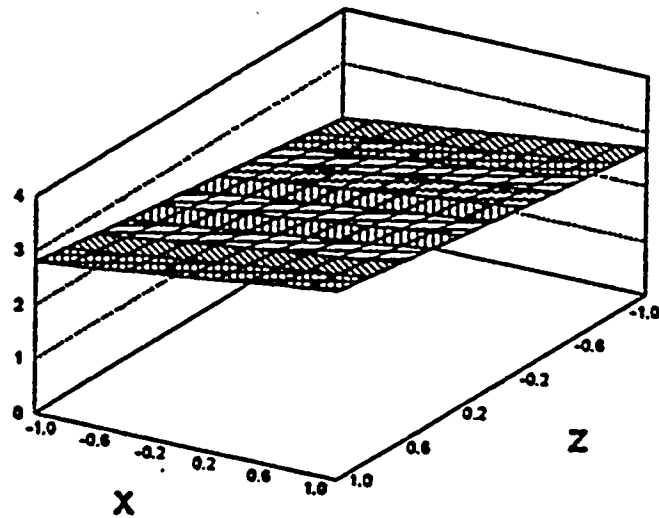


Corner Values
(X, Z)

(1,1)	= 4.9
(1,-1)	= 5.6
(-1,-1)	= 5.0
(-1,1)	= 4.3

Plotted vs Water Temperature (X) and Product Moisture (Z)

Figure 9. Particle Size for Black River Lime Hydrates.
 $D_{BRL} = 5.0 + 0.30 \times T_w$
 $- 0.35 \times W_{EX}$



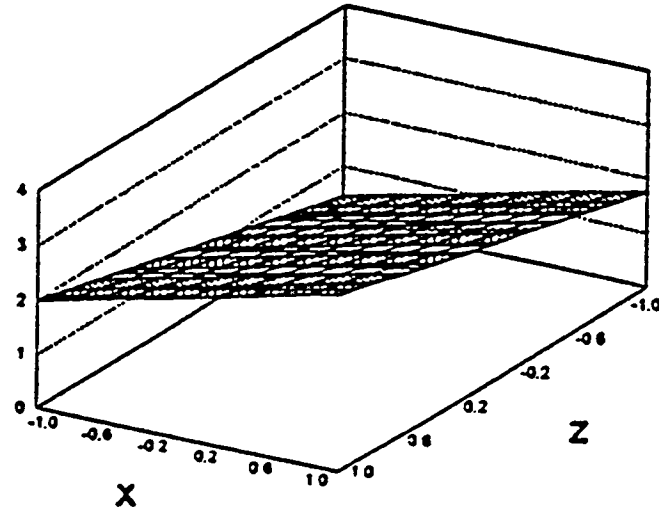
Corner Values
(X, Z)

(1,1)	= 3.5
(1,-1)	= 2.7
(-1,-1)	= 2.0
(-1,1)	= 2.8

Plotted vs Lime Feed Rate (X) and Product Moisture (Z)

Figure 10. Moisture Content for Mississippi Lime Hydrates.

$$W_{HL} = 2.7 + 0.34 \times L + 0.40 \times W_{EX}$$



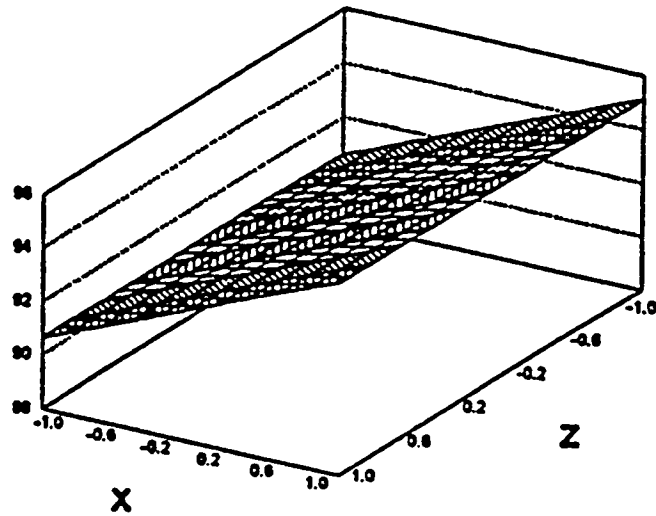
Corner Values
(X, Z)

(1,1)	= 3.3
(1,-1)	= 1.8
(-1,-1)	= 0.45
(-1,1)	= 2.0

Plotted vs Water Temperature (X) and Product Moisture (Z)

Figure 11. Moisture Content for Black River Lime Hydrates.

$$W_{BRL} = 1.9 + 0.65 \times T_w + 0.78 \times W_{EX}$$

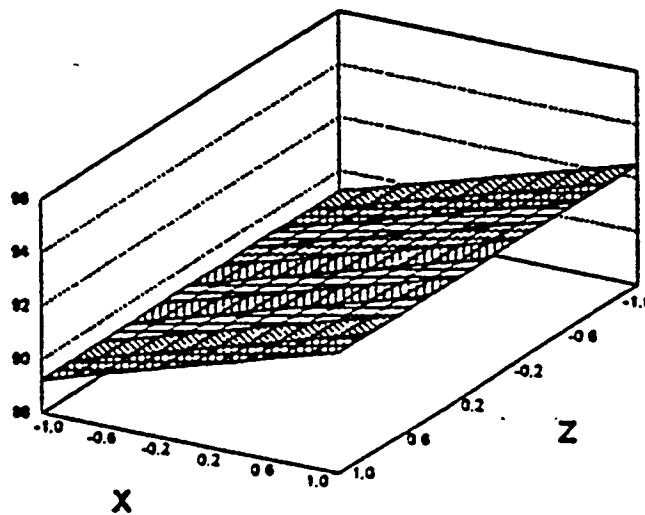


Corner Values (X, Z)	
(1,1)	= 95
(1,-1)	= 95
(-1,-1)	= 91
(-1,1)	= 91

Plotted vs Excess Water (X)

Figure 12. Content of Hydration for Mississippi Lime Hydrates.

$$H_{ML} = 93 + 2.3 \times W_{EX}$$

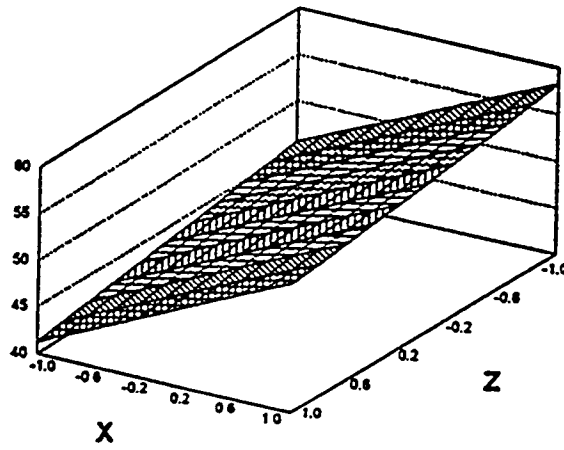


Corner Values (X, Z)	
(1,1)	= 93
(1,-1)	= 93
(-1,-1)	= 89
(-1,1)	= 89

Plotted vs Excess Water (X)

Figure 13. Content of Hydration for Black River Lime Hydrates.

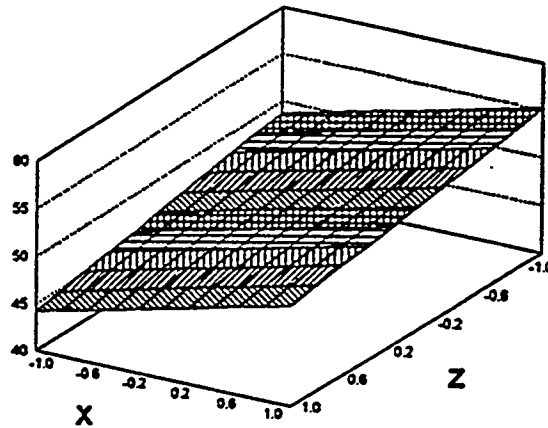
$$H_{BRL} = 91 + 1.6 \times W_{EX}$$



**Corner Values
(X, Z)**

(1,1)	= 54
(1,-1)	= 58
(-1,-1)	= 46
(-1,1)	= 41

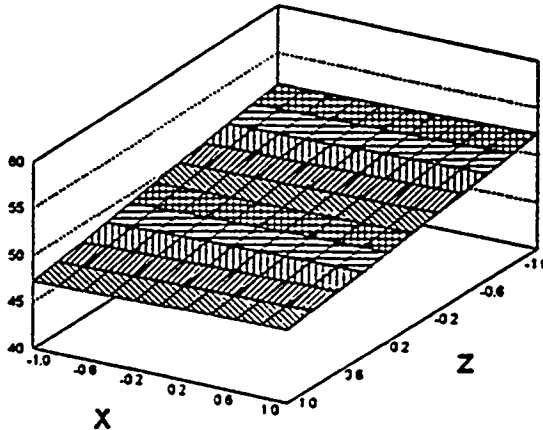
Plotted vs Lime Size (X) and Product Moisture (Z)
Water Temperature (-1), Held Constant



**Corner Values
(X, Z)**

(1,1)	= 51
(1,-1)	= 55
(-1,-1)	= 49
(-1,1)	= 44

Plotted vs Lime Size (X) and Product Moisture (Z)
Water Temperature (0), Held Constant



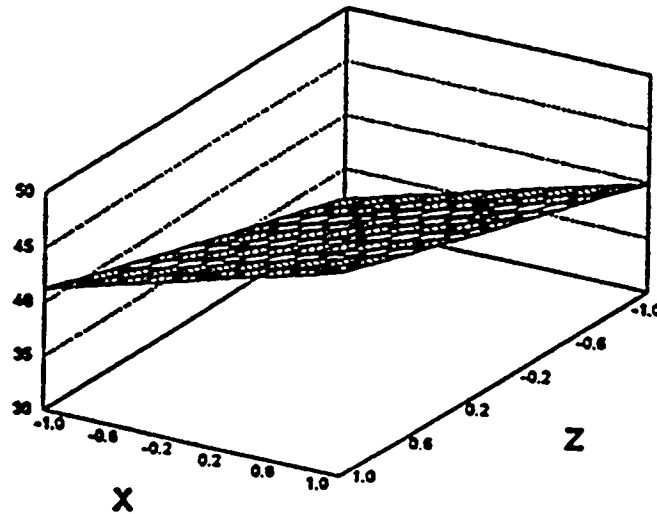
**Corner Values
(X, Z)**

(1,1)	= 48
(1,-1)	= 52
(-1,-1)	= 52
(-1,1)	= 47

Plotted vs Lime Size (X) and Product Moisture (Z)
Water Temperature (1), Held Constant

Figure 14. Calcium Utilization in Laboratory Tests
for Black River Lime Hydrates.

$$V_{BRL} = 50 + 3.2 \times D_{QL} - 3.0 \times D_{QL} \times T_W - 2.2 \times W_{EX}$$



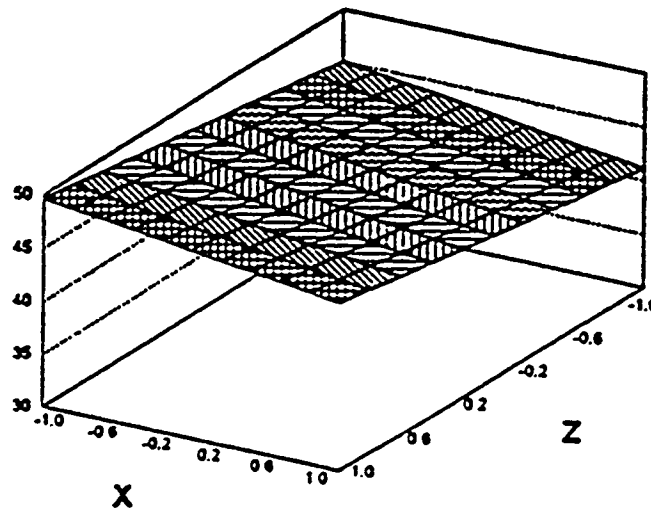
Corner Values
(X, Z)

(1,1)	= 49
(1,-1)	= 40
(-1,-1)	= 32
(-1,1)	= 41

Plotted vs Lime Size (X) and Product Moisture (Z)

Figure 15. Duct SO₂ Removal for Mississippi Lime Hydrates.

$$\Delta SO_2(ID)_{HL} = 40 + 3.8 \times D_{QL} + 4.4 \times W_{EX}$$



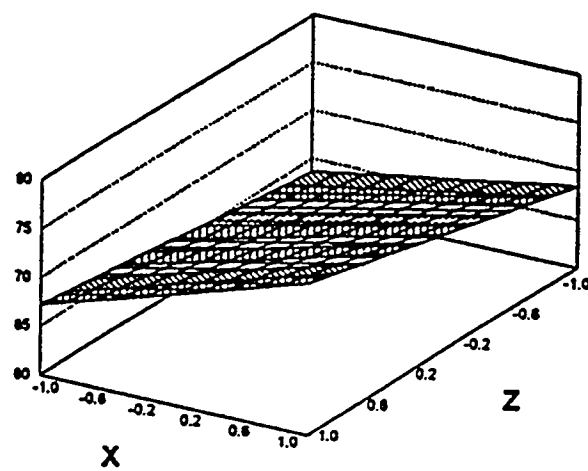
Corner Values
(X, Z)

(1,1)	= 46
(1,-1)	= 41
(-1,-1)	= 45
(-1,1)	= 50

Plotted vs Lime Size (X) and Product Moisture (Z)

Figure 16. Duct SO₂ Removal for Black River Lime Hydrates.

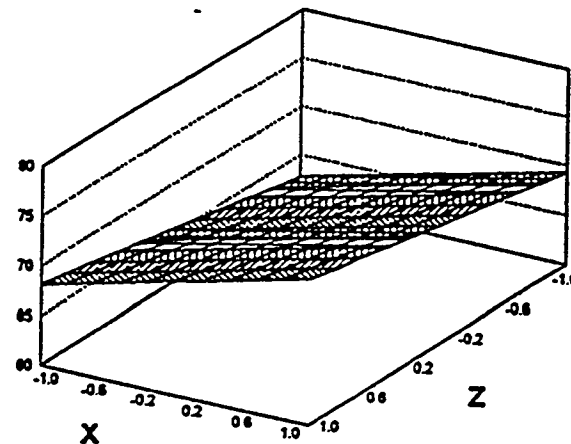
$$\Delta SO_2(ID)_{BRL} = 45 - 1.9 \times D_{QL} + 2.3 \times W_{EX}$$



**Corner Values
(X, Z)**

(1,1) = 75
(1,-1) = 68
(-1,-1) = 64
(-1,1) = 67

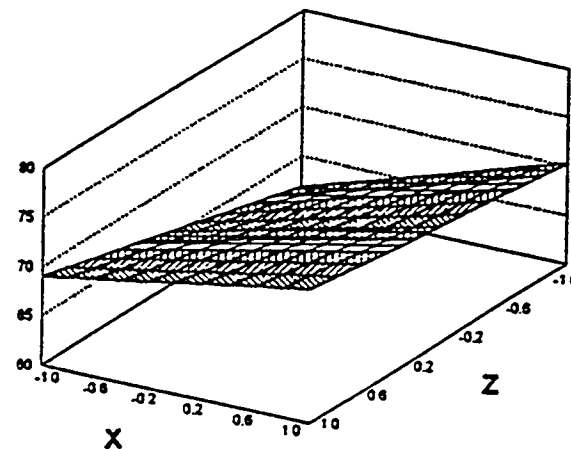
Plotted vs Lime Size (X) and Product Moisture (Z)
Water Temperature (-1), Held Constant



**Corner Values
(X, Z)**

(1,1) = 75
(1,-1) = 69
(-1,-1) = 63
(-1,1) = 68

Plotted vs Lime Size (X) and Product Moisture (Z)
Water Temperature (0), Held Constant



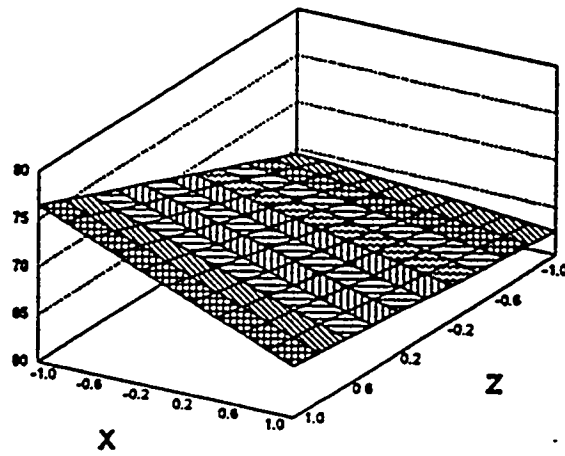
**Corner Values
(X, Z)**

(1,1) = 74
(1,-1) = 70
(-1,-1) = 62
(-1,1) = 69

Plotted vs Lime Size (X) and Product Moisture (Z)
Water Temperature (1), Held Constant

Figure 17. System SO₂ Removal for Mississippi Lime Hydrates.

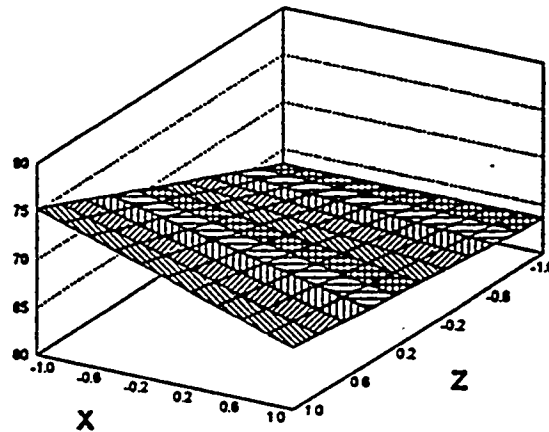
$$\Delta SO_2(S)_{ML} = 69 + 3.3 \times D_{QL} \\ + 2.6 \times W_{EX} \\ - 0.92 \times D_{QL} \times T_W \times W_{EX}$$



Plotted vs Lime Size (X) and Product Moisture (Z)
Water Temperature (-1), Held Constant

Corner Values
(X, Z)

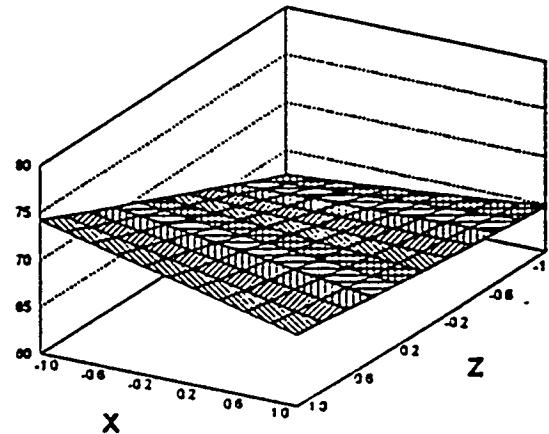
(1,1) = 66
(1,-1) = 63
(-1,-1) = 65
(-1,1) = 76



Plotted vs Lime Size (X) and Product Moisture (Z)
Water Temperature (0), Held Constant

Corner Values
(X, Z)

(1,1) = 67
(1,-1) = 64
(-1,-1) = 63
(-1,1) = 75



Plotted vs Lime Size (X) and Product Moisture (Z)
Water Temperature (1), Held Constant

Corner Values
(X, Z)

(1,1) = 68
(1,-1) = 65
(-1,-1) = 62
(-1,1) = 74

Figure 18. System SO₂ Removal for Black River Lime Hydrates.

$$\Delta \text{SO}_2(\text{S})_{\text{BRL}} = 67 + 2.1 \times D_{\text{ql}} + 1.1 \times D_{\text{ql}} \times T_{\text{w}} \\ + 3.7 \times W_{\text{EX}} \\ - 2.2 \times D_{\text{ql}} \times W_{\text{EX}}$$

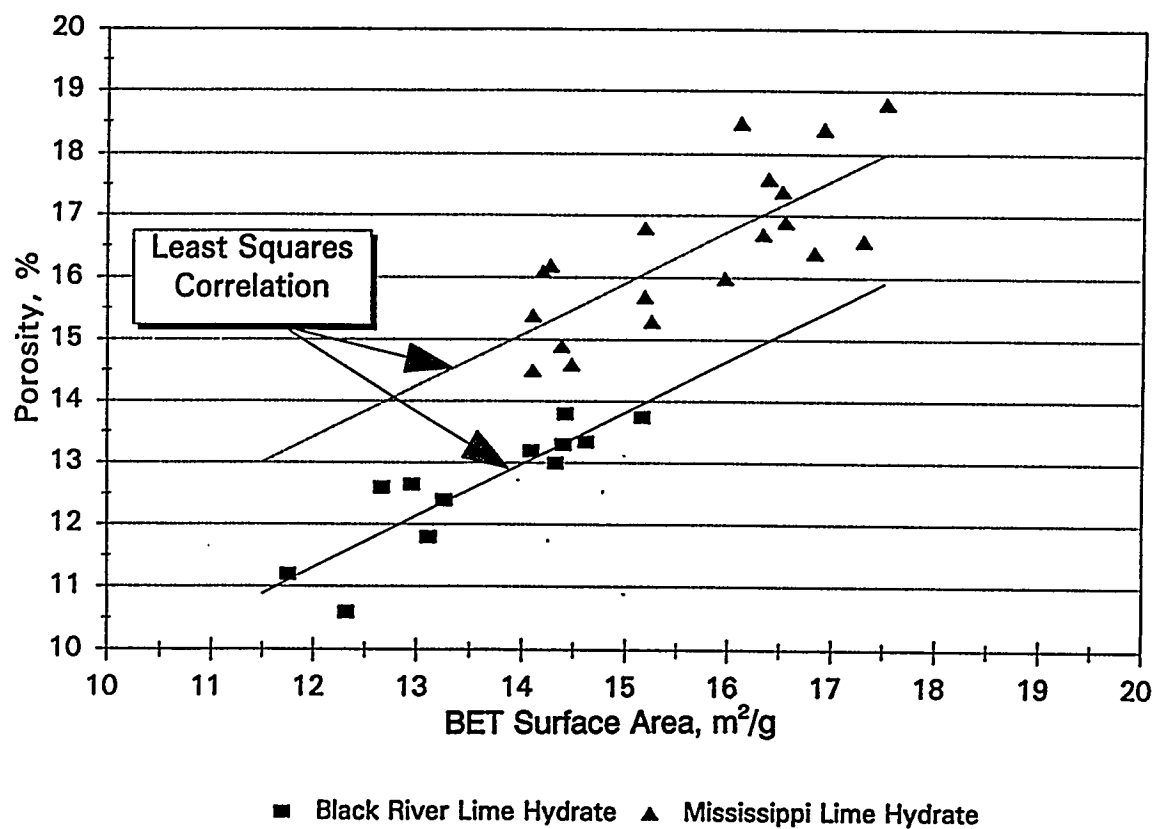


Figure 19. Hydrate Porosity-BET Surface Area Relationships.

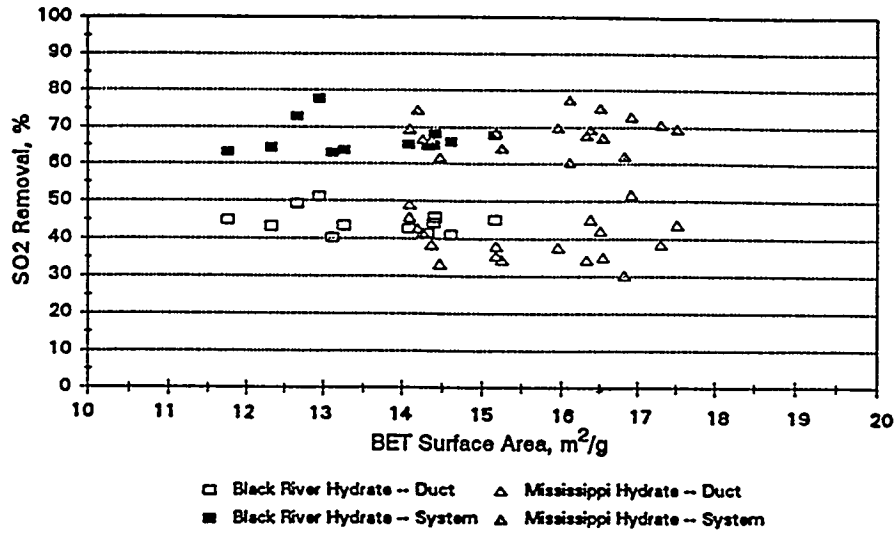


Figure 20. SO₂ Removals are Independent of BET Surface Area and Quicklime Source.

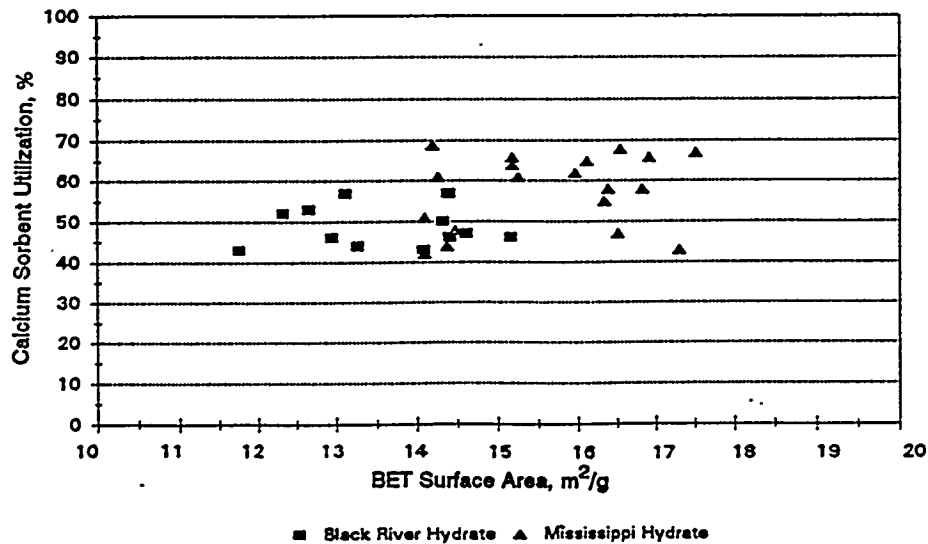


Figure 21. Calcium Utilization in Laboratory Tests is Independent of BET Surface Area and Quicklime Source.

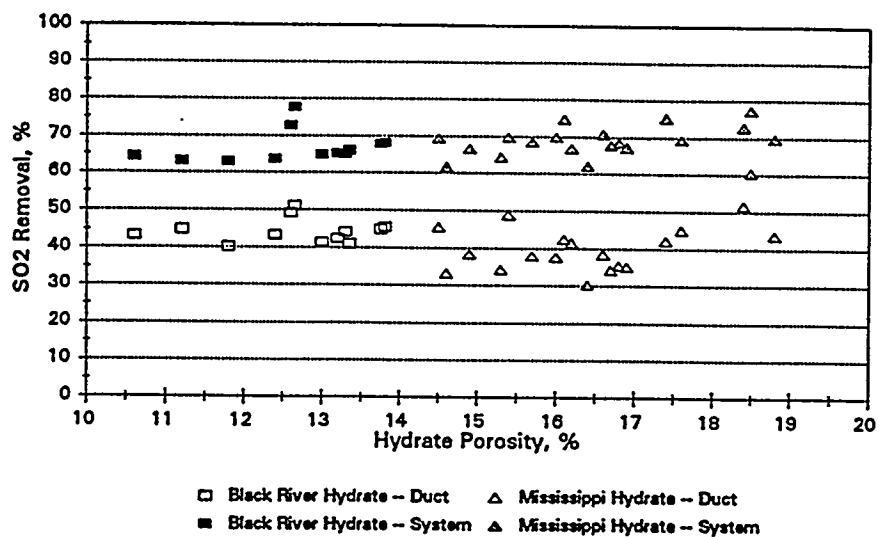


Figure 22. SO₂ Removals are Independent of Hydrate Porosity and Quicklime Source.

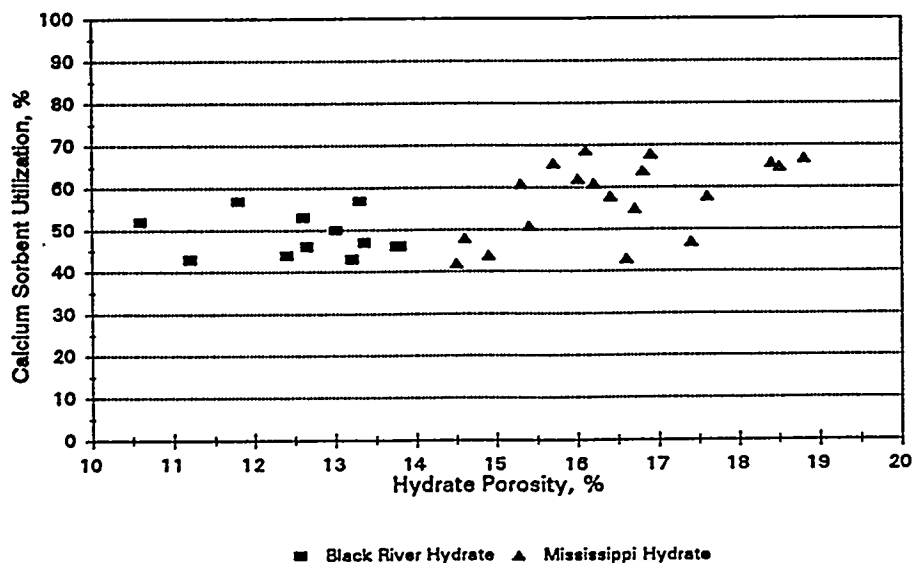


Figure 23. Calcium Utilization in Laboratory Tests is Independent of BET Hydrate Porosity and Quicklime Source.

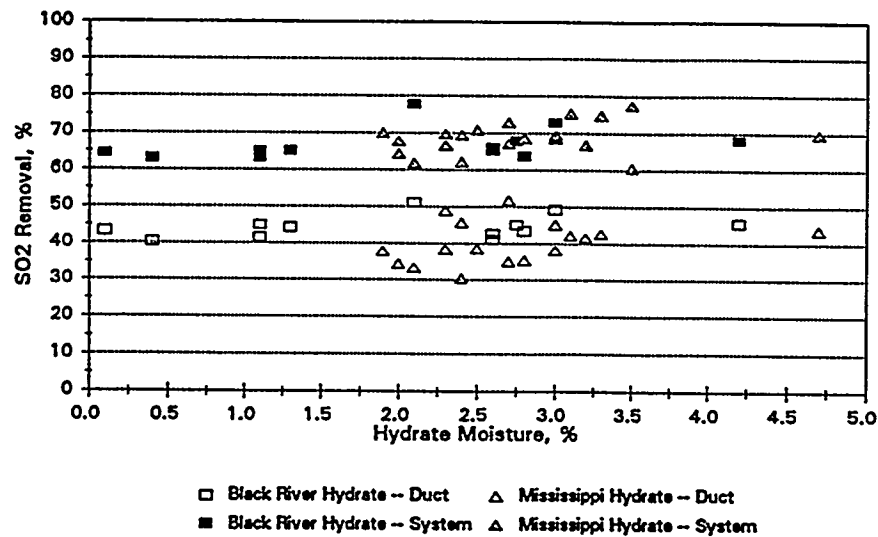


Figure 24. SO₂ Removals are Independent of Hydrate Moisture and Quicklime Source.

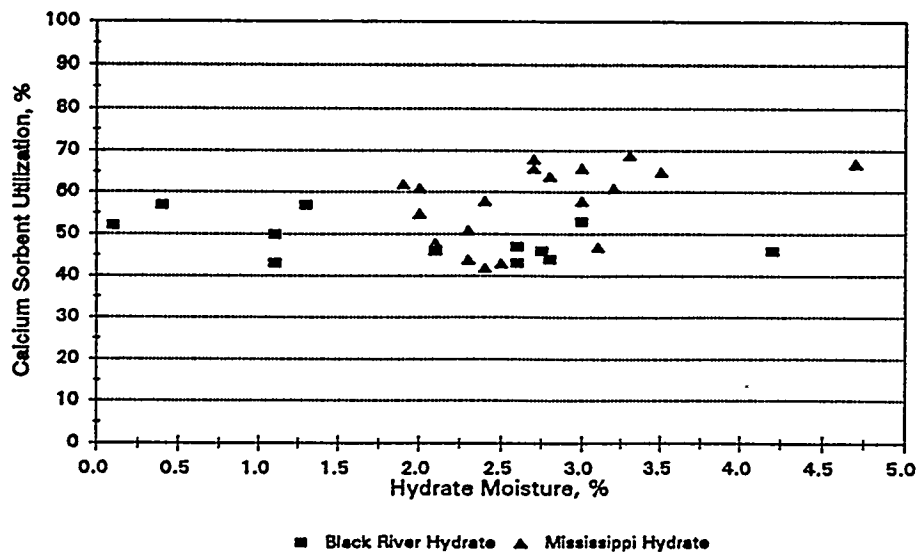


Figure 25. Calcium Utilization in Laboratory Tests is Independent of Hydrate Moisture and Quicklime Source.

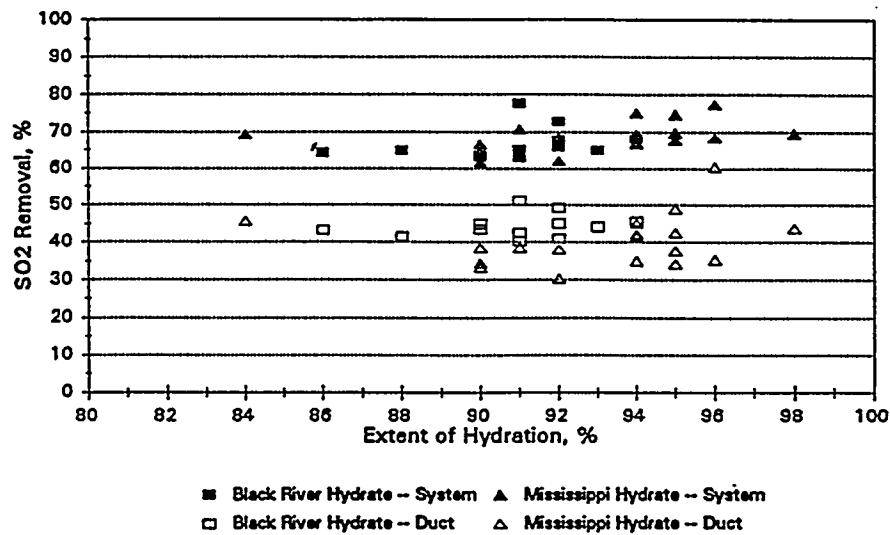


Figure 26. SO₂ Removals are Independent of the Extent of Hydration and Quicklime Source.

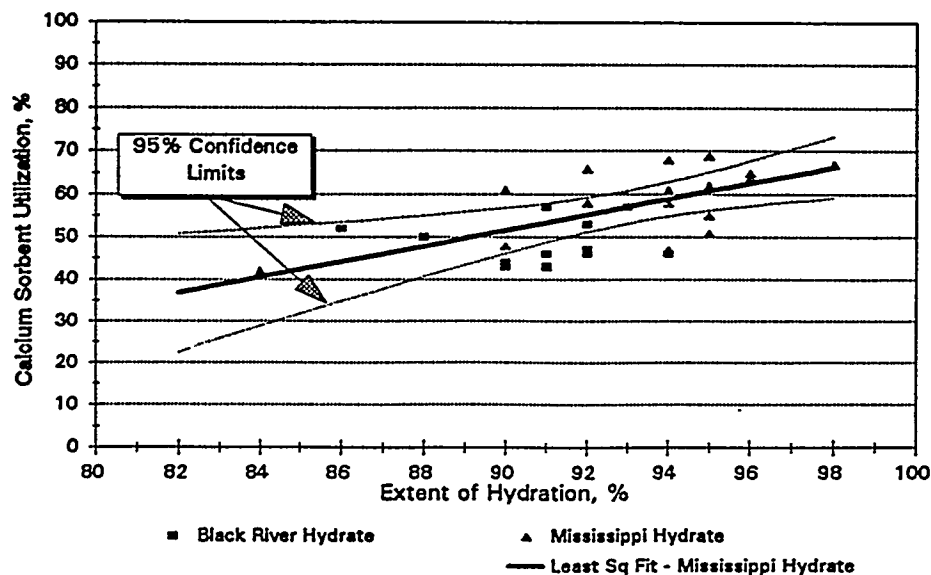


Figure 27. Calcium Utilization in Laboratory Tests is Independent of Hydration and Quicklime Source.